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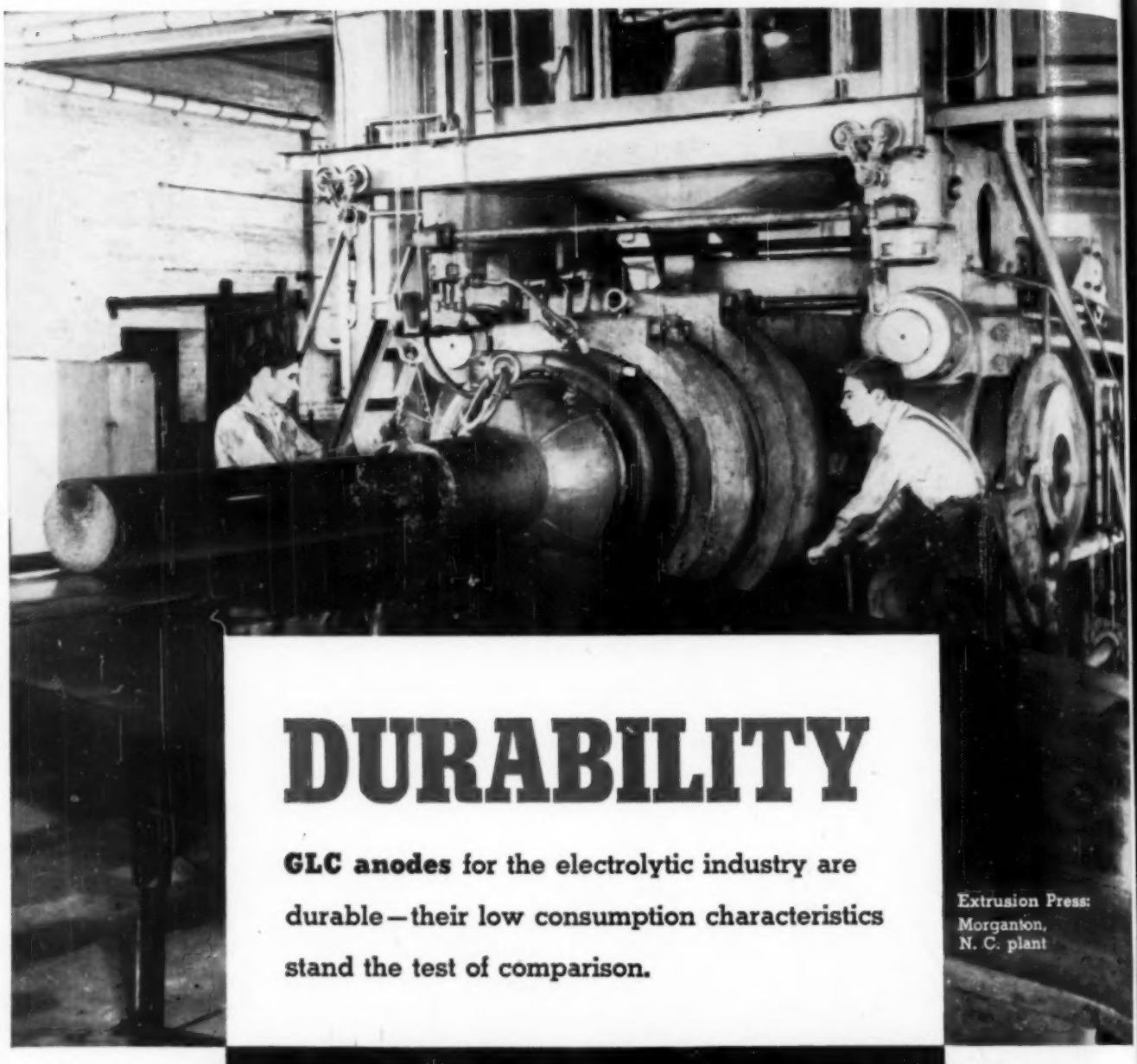

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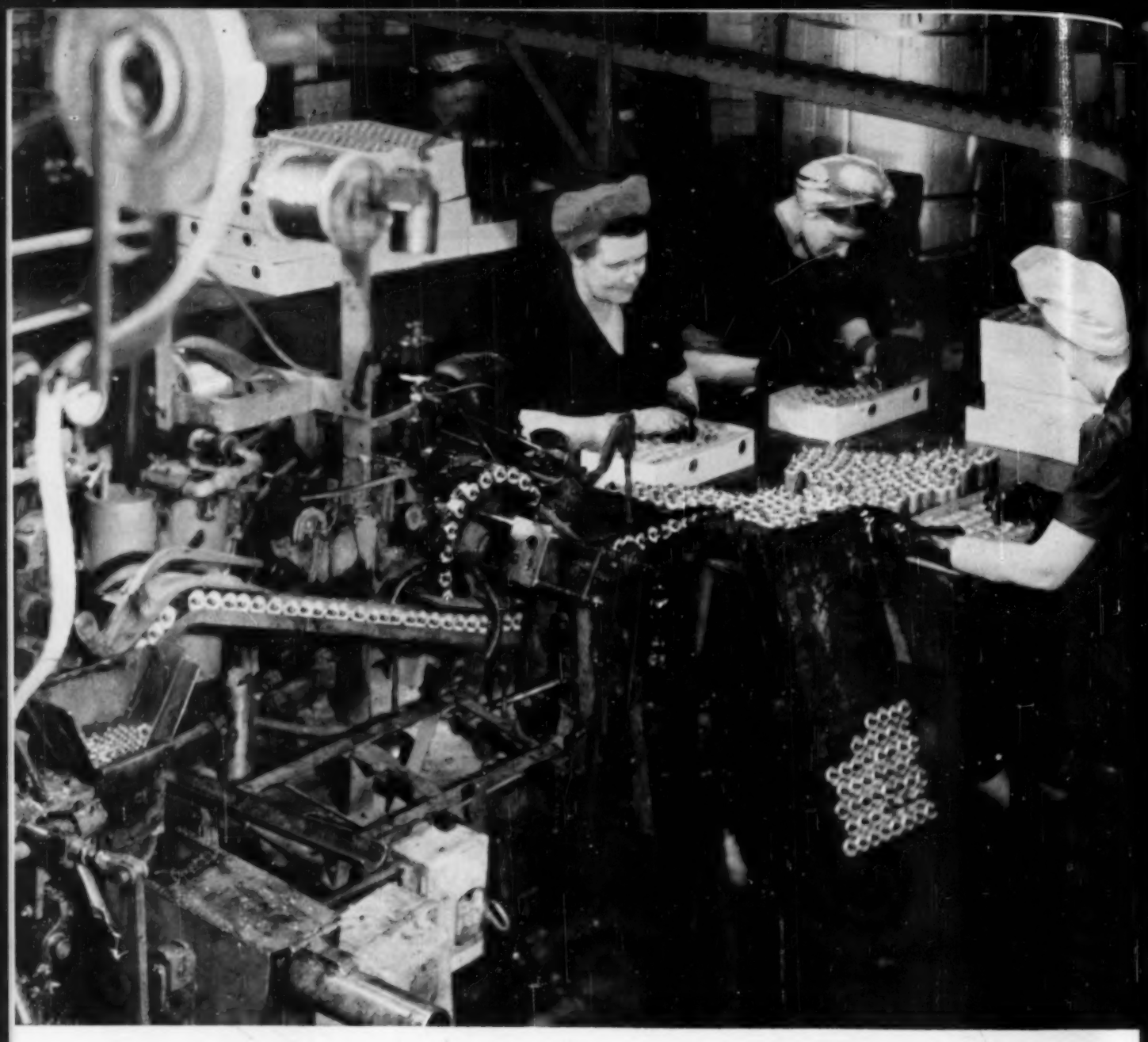

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A Proposed Mechanism for Self-Discharge of the Leclanché Cell[1]

CHARLES W. JENNINGS[2] AND W. C. VOSBURGH

Department of Chemistry, Duke University, Durham, North Carolina

ABSTRACT

A procedure was developed by which manganese dioxide electrodes can be reproduced within ±0.005 volt with manganese dioxide prepared by precipitation or by thermal decomposition of manganese (II) nitrate. Carbon mixed with either type of manganese dioxide lowers the electrode potential when exposed to electrolyte. The reaction involved is probably electrochemical; it takes place with electrical connection between dioxide and carbon instead of actual contact if these are in contact with the same electrolyte. The reaction is explained as the release of oxygen at the carbon surface by the oxidizing action of the manganese dioxide. This explanation was tested by measurement of the oxygen concentration in a solution originally oxygen-free, but in contact for some time with manganese dioxide and carbon.

INTRODUCTION

There are several possible processes by which a voltaic cell might deteriorate on open circuit. Although direct self-discharge by diffusion of one or both of the reactants of the cell reaction to the opposite electrode system is a theoretical possibility for any cell, the reactants of the Leclanché cell are not sufficiently soluble for this process to be of consequence. It has been pointed out (1) that the assumption once held of the presence of an appreciable concentration of tetravalent manganese compounds in the electrolyte is untenable. Hamer, Shrodt, and Vinal (2) showed that loss of water is an important cause of failure in dry cells, especially at high temperatures. They also showed that hydrogen is produced in the cell at a slow rate, but continuously. Reaction of the hydrogen, produced from zinc and electrolyte, with the manganese dioxide would be an indirect self-discharge process, but this reaction either does not take place at ordinary temperatures (3–5) or is very slow and would probably be retarded or inhibited by water (6). Reaction of manganese dioxide with ammonium ion and with carbon are both thermodynamically possible. It has been suggested that the former is important (7) but there was no detectable loss of available oxygen by manganese dioxide when heated with electrolyte or with carbon and electrolyte (8). Evidence was found of a small amount of reaction of manganese dioxide and carbon at higher temperatures (2). This was confirmed in preliminary experiments in this investigation, but the reaction is very slow and unimportant under the usual conditions. Much more important is another indirect self-discharge process for which evidence is presented in this paper. Manganese dioxide in contact with carbon and electrolyte can react electrochemically to deposit oxygen on the carbon. Desorption of this oxygen, its diffusion to the zinc, and reaction with the zinc complete the process.

EXPERIMENTAL

Preparation of manganese dioxide.—Two preparations of manganese dioxide, designated below as I-MnO_2 and II-MnO_2, were made by precipitation from acid solution. One liter of potassium permanganate solution, 73 g/l, was added to 500 ml of a solution of 104 grams of tetrahydrated manganese sulfate and 53 grams of sulfuric acid at 85°C. The precipitate of I-MnO_2 was washed with water by decantation, then with a dilute solution of ammonia and ammonium chloride, and finally with water again. It was filtered and dried at room temperature, 25° to 30°C. Analysis for available oxygen and total manganese gave a ratio of manganese to oxygen expressed by the fomula $MnO_{1.951}$.

Preparation II-MnO_2 differed from I-MnO_2 in that it was more thoroughly washed and was dried at 90°C. Analysis gave the formula $MnO_{1.967}$.

Preparation III-MnO_2 was deposited electrolytically on platinum wires from a solution of 50 g/l of tetrahydrated manganese sulfate and 67 g/l of sulfuric acid at a temperature of 85°C and a current density of 3 to 10 ma/cm^2.

Preparation IV-MnO_2 was made by decomposition of manganese nitrate at 200°C followed by

[1] Manuscript received June 22, 1951. This paper prepared for delivery before the Buffalo Meeting, October 11 to 13, 1950. Based on a thesis submitted by Charles W. Jennings in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University. This work was carried out under Contract N6ori-107 with the Office of Naval Research.

[2] Present address: Department of Chemistry, North Carolina State College, Raleigh, North Carolina.

heating in oxygen at 500°C. Analysis gave the formula $MnO_{1.988}$.

Preparation V-MnO_2 was reagent-grade commercial manganese dioxide that resembled IV-MnO_2 in appearance and was probably a synthetic material.

Preparation of the electrodes.—Manganese dioxide electrodes reproducible within a few millivolts could be made with precipitated manganese dioxide if this was first well digested with the electrolyte to be used. The usual treatment was to stir a suspension of the manganese dioxide in the electrolyte for 24 hours, then to separate the dioxide by suction filtration. The resulting paste of solid and electrolyte, with or without the addition of carbon or

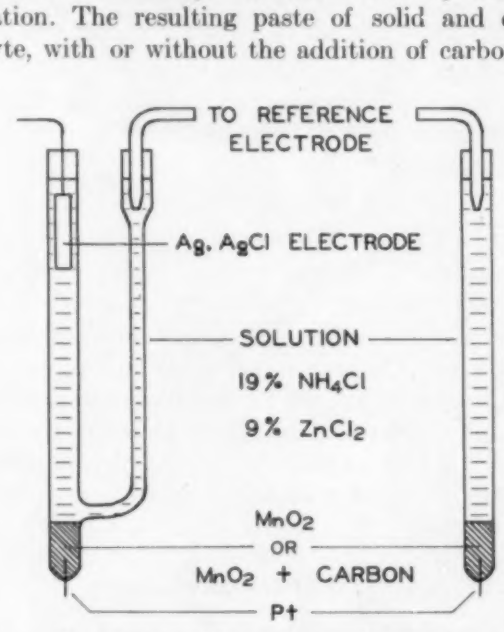

FIG. 1. Two forms of electrode vessel and the arrangement of the manganese dioxide electrode system.

other materials, was compressed around the platinum wire of the glass vessel of Fig. 1 with a pressure of about 500 lb/in.^{2} by means of a tightly fitting glass rod. The paste was then covered with electrolyte solution, and the electrode was ready for measurement. The electrolyte was either 4*N* ammonium chloride and 1.5*N* zinc chloride solution or 4*N* sodium sulfate and 1.5*N* zinc sulfate solution with a *p*H value of about 4.6 in most cases.

Measurements of the electrode potentials were made at room temperature against a silver, silver chloride, 1*N* potassium chloride reference electrode, which was 0.006 ± 0.0005 volt negative with reference to a saturated calomel electrode. Since a zinc-silver chloride cell has an electromotive force of a little over a volt, the electrode potentials can be converted approximately to the corresponding ones against a zinc electrode by the addition of one volt.

The digestion of the manganese dioxide with the electrolyte was important. Omission of this step led to much higher, less constant, and less reproducible electrode potentials. This is illustrated by the two curves for I-MnO_2 in Fig. 2, the lower of the two representing properly prepared electrodes.

At *p*H 7, electrodes prepared in the above manner were less satisfactory, and in more recent work an improved treatment has been devised.

Solubility of manganese dioxide in the electrolyte.—The possibility that an oxidizing agent such as Mn^{+4}, capable of causing self-discharge through diffusion, could exist in the electrolyte, was investigated experimentally. Some II-MnO_2 was stirred for 4 to 24 hours in an ammonium chloride-zinc chloride solution and samples were withdrawn for analysis at intervals. No more than $2 \cdot 10^{-5}$ equivalents/l of an oxidizing agent capable of oxidizing

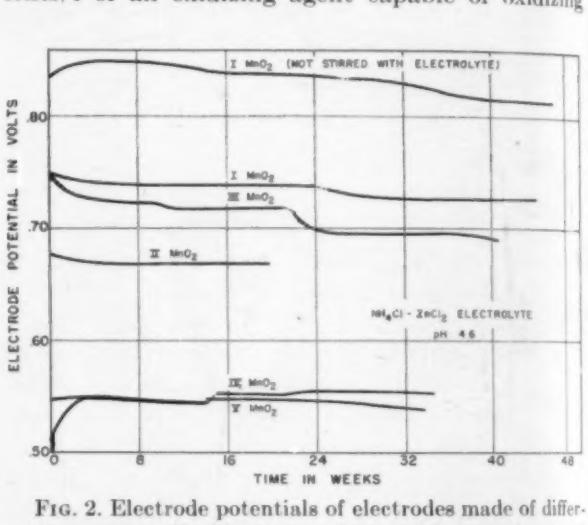

FIG. 2. Electrode potentials of electrodes made of different manganese dioxide preparations (without carbon) and their variation with time. Dashed portions indicate a change of electrolyte.

iodide ion was found by the analyses. Digestion of the dioxide and electrolyte at 100°C did not increase the concentration of oxidizing agent appreciably. The concentration of this oxidizing agent was too small to account for self-discharge of a dry cell by diffusion if the diffusion is assumed to take place in accordance with Fick's law, with a coefficient of the order of magnitude of 10^{-5}.

Reproducibility and Constancy of Electrodes and Effect of Different Manganese Dioxide Preparations

Electrodes were constructed of several manganese dioxide preparations with ammonium chloride-zinc chloride electrolyte at *p*H 4.6 to test the reproducibility of the electrodes and to provide a basis for comparison with electrodes containing other constituents. Variation of the average potentials of the electrodes with time is shown in Fig. 2. Each curve represents from one to five electrodes. The reproducibility of electrodes made with equiva-

lent amounts of material treated in the same way at any given time was within ±0.005 volt. Most electrodes varied little with time after once reaching a steady state. The breaks in the curves represent a change of electrolyte, usually with a slight increase in *p*H, since the acidity of the first electrolyte usually increased a little as the electrode aged.

Stirring the manganese dioxide with electrolyte prior to use in the electrode improved the reproducibility, and it also decreased the potential of the electrode considerably, as shown by the two I-MnO_2 curves of Fig. 2. Stirring decreased the *p*H of the electrolyte from 4.6 to 4.3, indicating a removal of some acid from the solid.

Large differences in potential were obtained with different forms of manganese dioxide. The unheated, chemically precipitated form (I-MnO_2) gave the highest potential. This type corresponds to the γ-MnO_2 obtained by Cole, Wadsley, and Walkley (9). More thorough washing and drying at 90°C (II-MnO_2) gave a lower potential. Electrodeposited manganese dioxide (III-MnO_2), also reported to be a γ-MnO_2 for the conditions of deposition employed (9, 10), had an initial potential near that of the precipitated material. Pyrolusite (IV-MnO_2) gave a much lower potential than the above types. A commercial preparation (V-MnO_2), crystalline in nature like pyrolusite, gave a potential close to that of IV-MnO_2.

Effect of Carbon

When carbon was mixed with the paste of manganese dioxide and electrolyte the electrodes had a lower potential than those without carbon. The potential of such electrodes decreased as the ratio of carbon to dioxide increased, as shown in Fig. 3. Except as otherwise noted, the carbon throughout the investigation was 50 per cent compressed Shawinigan acetylene black.[3] In Fig. 3 the ratios are those of the volume of wet manganese dioxide to the volume of dry carbon. They are approximate and only indicate the effect of the amount of carbon. In subsequent data when the ratio of manganese dioxide to carbon is not indicated, it is one to one.

The curves of Fig. 3 show a general pattern for the electrodes containing carbon. A large initial decrease in the potential occurs within a few hours (before the first measurement), followed by a slower decrease for a few weeks, and then a very slow decrease for the remainder of the period of observation.

Preliminary treatment of the carbon with an acid permanganate solution, or heating above 500°C for 15 minutes prior to mixing with the manganese dioxide, did not prevent it from lowering the potential of a manganese dioxide electrode. This indicates that the change in potential is not caused by the presence of oxidizable impurities, but must be attributed to the carbon itself.

Lowering of the electrode potential by carbon is not restricted to Shawinigan black. Other forms of carbon, namely graphite (both a highly purified variety prepared for spectroscopic use, and the ordinary commercial powdered form), Norite (activated carbon), and carbon taken from a commercial air cell, showed a similar effect. The effects of the various kinds of carbon were not of the same magnitude, however, as shown by Fig. 4. The curves represent the potentials of electrodes made from mixtures of 0.3 gram of carbon and 3 grams of wet

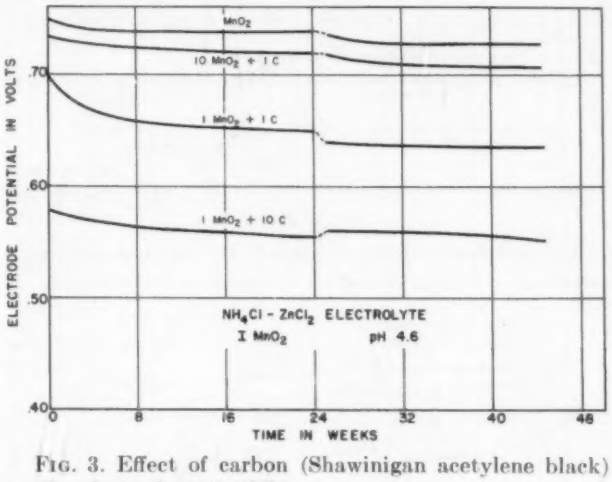

FIG. 3. Effect of carbon (Shawinigan acetylene black) on the electrode potential.

manganese dioxide. The amount of lowering varies directly with the probable adsorptive capacity of the carbon.

Three different types of manganese dioxide, when mixed with carbon, gave electrodes with lower potentials than those without carbon as shown in Fig. 5. The effect of carbon is not as great with pyrolusite (IV-MnO_2) as with the precipitated material (I-MnO_2), but appears to depend, qualitatively at least, on the potential of the electrode. The effect was very pronounced with the manganese dioxide electrodeposited on the platinum wire (III-MnO_2), because there was a small amount of manganese dioxide in contact with a relatively very large amount of carbon.

Little difference was found between electrodes with ammonium chloride-zinc chloride electrolyte and those with sodium sulfate-zinc sulfate electrolyte at the same *p*H, either with or without carbon. When the *p*H of the electrolyte was increased from 4.6 to 7.3 by the addition of ammonia, the electrodes with carbon still had a lower potential than those without carbon.

[3] Obtained through the courtesy of Shawinigan Products Corporation.

The potential of an electrode in which the carbon was separated from the manganese dioxide by an asbestos layer was not at all affected by the carbon.

In an electrode of the type shown in Fig. 6 the carbon lay on top of the manganese dioxide with one platinum wire in contact with carbon only and other wires at different levels in the dioxide. Not only the dioxide in direct contact with the carbon,

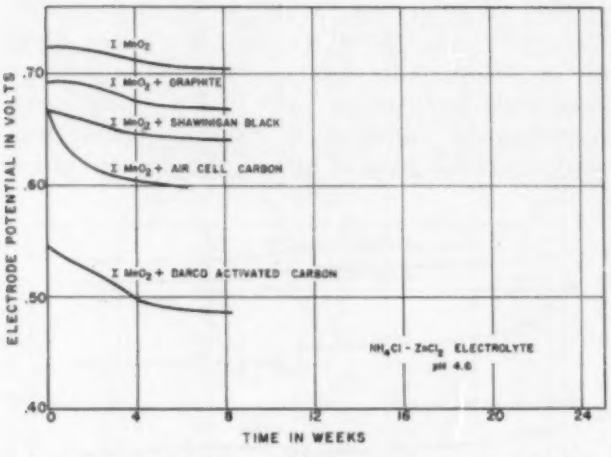
ELECTRODE POTENTIAL IN VOLTS
TIME IN WEEKS
I MnO2
I MnO2 + GRAPHITE
I MnO2 + SHAWINIGAN BLACK
I MnO2 + AIR CELL CARBON
I MnO2 + DARCO ACTIVATED CARBON
NH4Cl - ZnCl2 ELECTROLYTE
pH 4.6

FIG. 4. Effect of different kinds of carbon on the electrode potential; 0.3 gram of carbon to 3 grams of wet MnO_2.

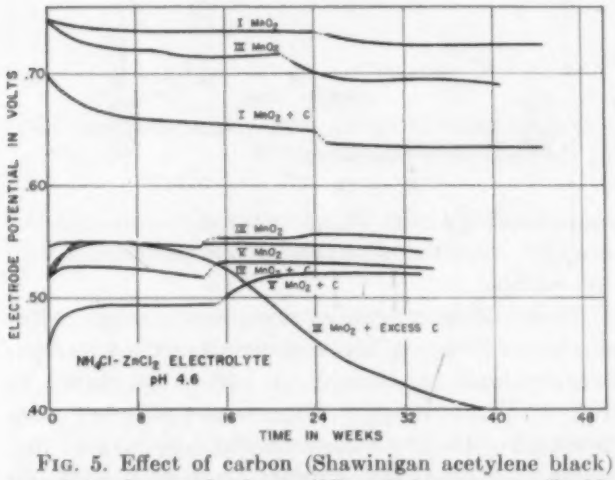

FIG. 5. Effect of carbon (Shawinigan acetylene black) on electrodes made from different manganese dioxide preparations; ratio of carbon to MnO_2 approximately one to one except with III-MnO_2.

but also that at a distance from the carbon, decreased in potential. The decrease at a distance from the border became larger with time. The potential of the electrode near the carbon border decreased at first, but then increased slowly with time. It soon became equal to the potential of the carbon, and the potentials of all electrodes slowly approached a common value for the remainder of the period of observation.

The decrease in potential of electrodes A and B of Fig. 6 with time can be explained by what has been called rearrangement (11). Suppose the dioxide at the borderline becomes partially reduced (see later), then by the rearrangement process the reduction slowly travels downward. The potential of an electrode of carbon and electrolyte is about 0.3 volt, but because of its good conductivity all of the carbon soon acquires the potential of the dioxide at the point of contact with the carbon.

The behavior of this electrode system, in which there is only limited physical contact between the manganese dioxide and carbon, suggests that there may be a reaction of an electrochemical nature between the dioxide and carbon to account for the changes in potential.

Carbon had little if any effect in lowering the potential of an electrode of manganese oxyhydroxide (MnOOH) and electrolyte.

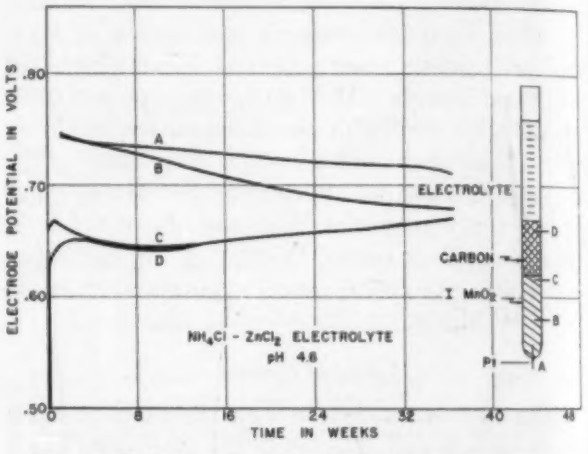

FIG. 6. Experiment with carbon above the manganese dioxide and multiple platinum electrodes (A, B, C, and D) at different levels.

Two other conductors thought to be inert toward manganese dioxide were tried in place of carbon. An electrode of I-MnO_2 and finely divided gold in either the chloride or sulfate electrolyte behaved like one of carbon and I-MnO_2. An electrode of precipitated platinum black and the chloride electrolyte gave a much lower potential than any of the electrodes with carbon and I-MnO_2. The potential decreased rapidly with time and became negative with respect to the reference electrode. Replacement of the chloride electrolyte with the sulfate gave an electrode that behaved like one with a high ratio of carbon to dioxide. Longer length of smooth platinum wire in contact with the dioxide had no effect on the potential of an electrode. This suggests that the finely divided platinum acts as a catalyst of some reaction in the chloride electrolyte, possibly the oxidation of ammonium ion by the dioxide.

If there is a reaction of an electrochemical nature between carbon and manganese dioxide when they

are in physical contact, there should be a reaction also when they are physically separated but in electrical contact. A cell was made of separate manganese dioxide and carbon electrodes connected by a salt bridge of electrolyte. A minimum amount of carbon was added to the manganese dioxide electrode. This cell gave a measurable current when the platinum contacts of the electrodes were connected through a microammeter. The current passed from the positive manganese dioxide to the negative carbon and decreased to a small value as both electrodes approached the same potential. When the connection was broken the carbon electrode decreased in potential with time, approaching its initial value of 0.3 volt while the manganese dioxide potential increased slightly with time. Little change in the behavior of the cell was found when the sulfate electrolyte was substituted for the chloride electrolyte. The greater the amount of carbon in the carbon electrode, the greater was the current obtained, and the greater the decrease in potential of the dioxide electrode. This is similar to the effect noted when carbon was added directly to the manganese dioxide in the electrode vessel.

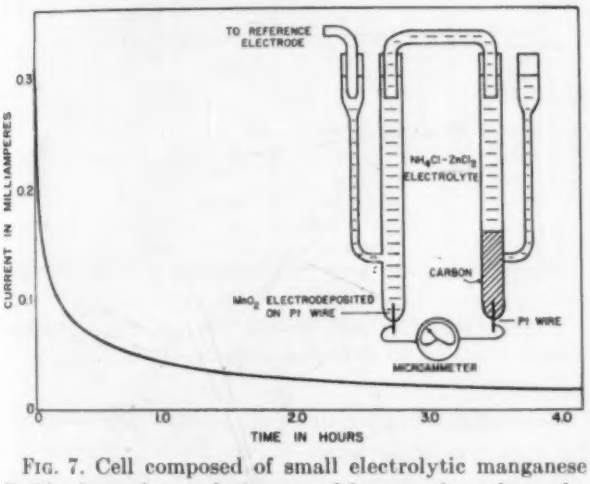

FIG. 7. Cell composed of small electrolytic manganese dioxide electrode on platinum and large carbon electrode, and its discharge curve.

Fig. 7 illustrates a more quantitative variation of this experiment. An electrode made by electrodeposition of manganese dioxide on a platinum wire (III-MnO_2) using a total of 2.5 ma-hr of electricity was connected to a carbon electrode containing a large amount of carbon. The potential of the dioxide electrode decreased from 0.66 volt to 0.48 volt in four hours, while that of the carbon increased from 0.26 to 0.48 volt. The discharge curve is shown in Fig. 7. About 0.16 ma-hr was obtained in the four hours. On the basis of a theoretical capacity of 1.25 ma-hr (for discharge to MnOOH) 13 per cent of the capacity of the manganese dioxide was consumed in four hours. Over a longer period of time the discharge continued slowly. This experiment, although made with a very large ratio of carbon to manganese dioxide, showed that the latter can be reduced electrochemically by carbon.

This was demonstrated in another way. Two electrodes were made by electrodeposition of manganese dioxide on pure graphite rods under the same conditions as for III-MnO_2. One was immersed in electrolyte and connected to a bare graphite rod, also immersed in the electrolyte, for 24 hours. Then both of the manganese dioxide electrodes were discharged in combination with zinc electrodes through external resistance which was adjusted to give an initial current of 0.8 ma or 0.1 ma/cm² of surface. The dashed lines in Fig. 8 give the current and voltage changes on discharge of the electrode that had been connected to the graphite rod. The continuous curves are the corresponding curves for the control electrode which was not so treated. This experiment was typical of several; electrodes that had been connected to carbon gave considerably less energy on discharge than control electrodes. Both the preparation of the electrodes and the discharges were carried out essentially as described by Ferrell and Vosburgh (11).

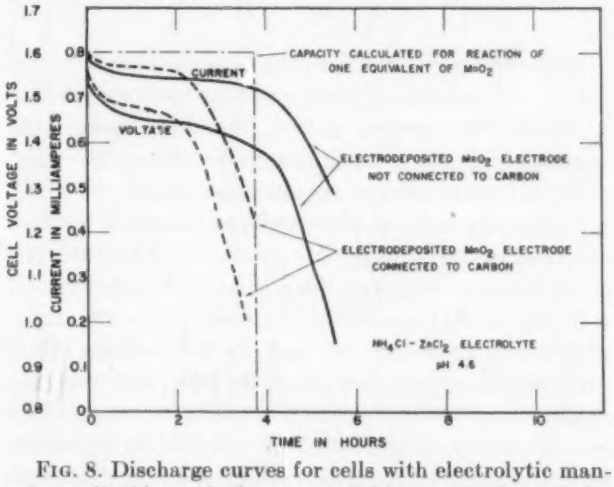
CAPACITY CALCULATED FOR REACTION OF ONE EQUIVALENT OF MnO_2
CURRENT
VOLTAGE
ELECTRODEPOSITED MnO_2 ELECTRODE NOT CONNECTED TO CARBON
ELECTRODEPOSITED MnO_2 ELECTRODE CONNECTED TO CARBON
$NH_4Cl - ZnCl_2$ ELECTROLYTE
pH 4.6
CELL VOLTAGE IN VOLTS
CURRENT IN MILLIAMPERES
TIME IN HOURS

FIG. 8. Discharge curves for cells with electrolytic manganese dioxide cathodes (on graphite) and zinc anodes showing effect of previous connection of the cathode with a graphite rod in presence of electrolyte.

Discussion of the effect of carbon.—There are few possibilities for oxidation at the carbon electrode. The most probable reaction is the liberation of oxygen. At the electrode potentials involved, the oxygen would be adsorbed by the carbon, probably by formation of a loose complex with the carbon, instead of being liberated as a gas. Carbon is known to have considerable capacity for adsorption of oxygen, and different carbons differ in their capacity

for adsorption, hence the differences shown in Fig. 4.

The reactions involved in the liberation of oxygen can be explained best in terms of a carbon-manganese dioxide cell. In this cell, the reaction

$$e^- + H^+ + MnO_2 \rightarrow MnOOH$$

may be assumed to take place at the positive and

$$H_2O + C \rightarrow C(O) + 2H^+ 2e^-$$

at the negative, to give a net reaction of

$$2MnO_2 + C + H_2O \rightarrow C(O) + 2MnOOH.$$

The potential of the carbon electrode originates from the oxygen present. Krivolutskaya, Temerin, and Lukovtsev (12) found that graphite that had been evacuated to 10^{-5} mm of mercury at 410°–420°C gave an electrode with a negative potential with respect to a saturated calomel electrode as compared with about +0.3 volt for ordinary graphite.

Any process that causes the oxygen to be removed from the carbon, or that renders the oxygen unavailable for further action, should decrease the potential of the carbon electrode. When the electrode is connected to a manganese dioxide electrode, any oxygen lost can be replaced through further electrochemical action. One process by which oxygen could be removed from the carbon is desorption and solution of the oxygen in the electrolyte. By diffusion away it would be lost to the carbon. This process would be expected to be slow, and the rate might vary with different types of carbon. The slow decrease in potential of the carbon electrode on disconnection from the manganese dioxide electrode is understandable on the basis of this process.

The same type of electrochemical action as in the manganese dioxide-carbon cell can be considered to occur when carbon and the dioxide are mixed with electrolyte and compressed in the electrode vessel. Here, however, they are in close contact and the solution path is very short so that the action is more rapid. This would account for the rapid initial decrease in potential of a manganese dioxide electrode on addition of carbon. The variation with the amount of carbon present is understandable, since the greater the amount of carbon present, the greater the capacity for taking on oxygen. The very slow decrease in potential observed for manganese dioxide electrodes, with or without carbon, after reaching steady-state conditions, indicates only a very slow loss of oxygen under these conditions. The desorption and solution of oxygen would be expected to take place until the oxygen reaches its equilibrium concentration in the electrolyte. Any means by which the oxygen is removed from the solution would cause a continued decrease in potential and loss in capacity of the electrode. Winslow (13) observed no oxidation of carbon by oxygen dissolved in acid solutions at concentrations corresponding to oxygen pressures below 447 mm.

Effect of Zinc

When a piece of zinc wrapped in filter paper was placed on top of the mixture of manganese dioxide and carbon in an electrode, the potential decreased faster than a similar electrode with filter paper but without zinc as shown in Fig. 9. This figure also shows that without carbon there is also a decrease, but a slower one.

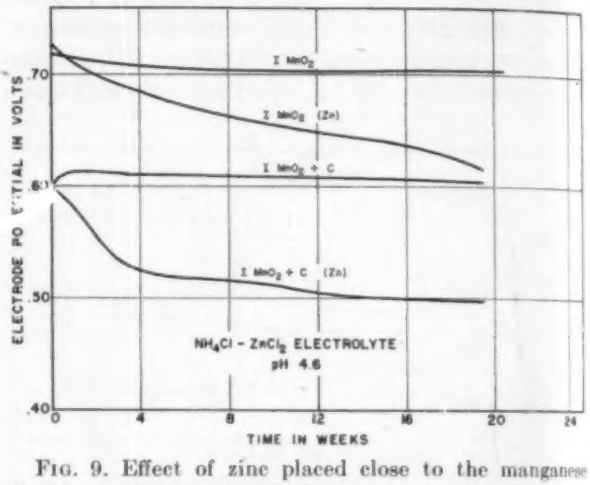

FIG. 9. Effect of zinc placed close to the manganese dioxide, but not in electrical contact with it.

Zinc might cause a decrease in electrode potential by reaction with acid, which would increase the *p*H. However, even an increase in *p*H large enough to cause diammine zinc chloride to precipitate would not be enough to account for the decrease in potential observed. Daniel-Bek (14) observed that the corrosion of zinc in an electrolyte is increased by the presence of manganese dioxide even when this is not in contact with the zinc.

Test for Oxygen

If the formation and release of oxygen is the correct explanation of the loss in potential and capacity of a manganese dioxide electrode, then it should be possible to detect oxygen in a solution previously freed of it and in contact with manganese dioxide and carbon. Analyses were made of the oxygen content of such solutions by a voltammetric method with the use of a stationary platinum microelectrode instead of a dropping mercury electrode and a large silver-silver chloride electrode as the anode (15).

Several arrangements of manganese dioxide and carbon were used. In all cases the diffusion current, a measure of the oxygen content, increased when a

solution previously freed from oxygen was placed in contact with manganese dioxide and carbon, or carbon that had been in contact with manganese dioxide. One such arrangement is shown in Fig. 10. In the upper chamber were placed carbon rods half covered with electrolytic manganese dioxide and tied in a bundle by a platinum wire. A dilute solution of ammonium and zinc chlorides was freed from oxygen by a stream of nitrogen and then forced up into the upper chamber. Then a series of measurements of current and voltage between the platinum

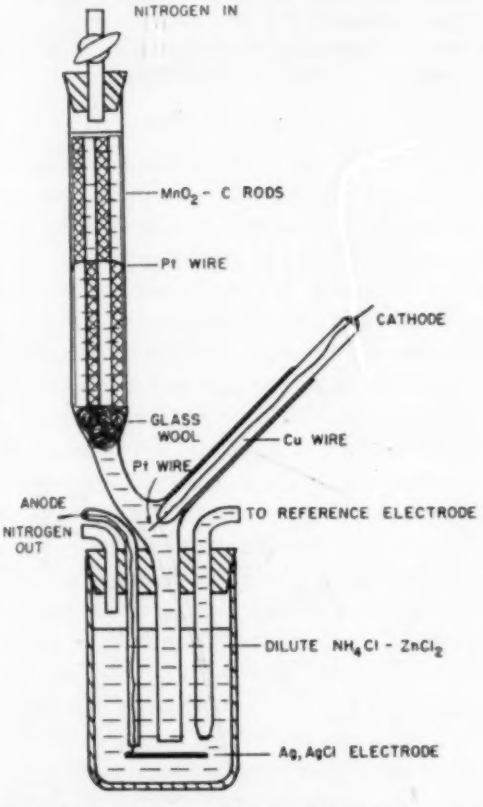

FIG. 10. Apparatus for voltammetric test for oxygen in a solution previously in contact with manganese dioxide and carbon.

and silver electrodes was made for a blank. After a period in contact with the rods the solution in the upper chamber was allowed to fall so that it would be in contact with the platinum electrode, and the current-voltage curve was again determined. The results are shown in Fig. 11. The lowest curve is for the air-free solution. The two highest, dashed curves are calibration curves with the solution saturated with air. Obviously the method does not give good reproducibility. However, the solid curves for a solution originally air-free that had been in contact with the rods in the upper chamber show an oxygen content of the order of magnitude of that of a solution saturated with air. The higher curve was for fresh electrodes, the lower a second determination after expulsion of the oxygen of the first. The contact with the rods was shorter in the second determination, and there is no assurance that either of the curves represents the maximum oxygen concentration attainable. It was considered sufficient for the present to demonstrate a concentration comparable to that of an air-saturated solution. This is large enough to account for an appreciable rate of diffusion from one electrode to the other of a dry cell.

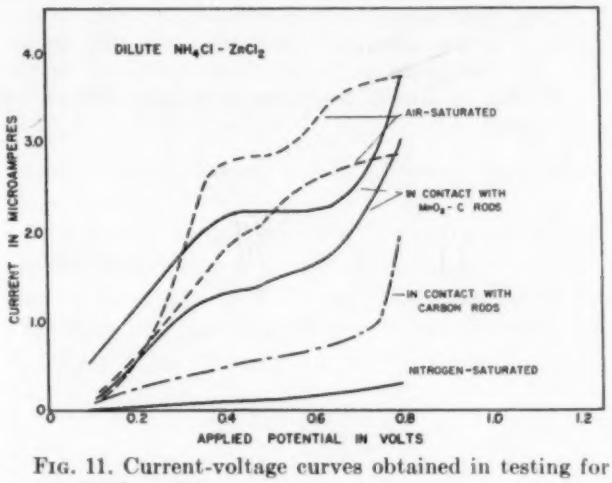

FIG. 11. Current-voltage curves obtained in testing for oxygen in electrolyte.

CONCLUSION

An explanation of one self-discharge process in the dry cell can now be suggested. Manganese dioxide, in contact with solution and with carbon, causes oxygen to be deposited on the carbon. In so doing, the manganese dioxide becomes reduced, and the potential of the electrode system decreases. Part of the oxygen on the carbon is desorbed, probably slowly, and diffuses to the zinc where it reacts. The oxygen lost from the carbon is replaced by further reduction of the manganese dioxide. Oxygen may also be lost from an active type of manganese dioxide directly to the solution at a slow rate. In the usual form of the dry cell it is only necessary for the diffusion of the oxygen to take place across the short distance from the exterior of the bobbin to the zinc in order to discharge the entire bobbin in time.

In the self-discharge of the dry cell by this oxygen-diffusion process, different types of carbon with different capacities for adsorption, and perhaps different rates of desorption, and different types of manganese dioxide with different potentials and structures, would be expected to give different lengths of shelf life.

ACKNOWLEDGMENT

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Any discussion of this paper will appear in a Discussion Section, to be published in the June 1953 issue of the JOURNAL.

REFERENCES

1. C. DROTSCHMANN, *Z. Elektrochem.*, **54**, 306 (1950).
2. W. J. HAMER, J. P. SCHRODT, AND G. W. VINAL, *Trans. Electrochem. Soc.*, **90**, 449 (1946).
3. N. K. CHANEY, *Trans. Electrochem. Soc.*, **29**, 320 (1916).
4. F. DANIELS, *Trans. Electrochem. Soc.*, **53**, 45 (1928).
5. W. A. WHITSELL AND J. C. W. FRASER, *J. Chem. Soc.*, **45**, 2847 (1923).
6. J. C. W. FRASER AND C. E. GREIDER, *J. Phys. Chem.*, **29**, 1101 (1925).
7. F. MULLER AND H. REUTHER, *Z. Elektrochem.*, **47**, 177 (1941).
8. E. OTTO, G. W. VINAL, AND E. H. OSTRANDER, *Trans. Electrochem. Soc.*, **86**, 327 (1944).
9. W. F. COLE, A. D. WADSLEY, AND A. WALKLEY, *Trans. Electrochem. Soc.*, **92**, 133 (1947).
10. H. F. MCMURDIE, *Trans. Electrochem. Soc.*, **86**, 313 (1944).
11. D. T. FERRELL, JR., AND W. C. VOSBURGH, *J. Electrochem. Soc.*, **98**, 334 (1951).
12. N. S. KRIVOLUTSKAYA, S. A. TEMERIN, AND P. D. LUKOVSTEV, *J. Phys. Chem.* (*U.S.S.R.*), **21**, 313 (1947).
13. N. M. WINSLOW, *Trans. Electrochem. Soc.*, **92**, 422 (1947).
14. V. S. DANIEL-BEK, *J. Applied Chem.* (*U.S.S.R.*), **13**, 1572 (1940), cited by C. DROTSCHMANN, "Trockenbattieren," p. 74, Becker and Erler Kom.-Ges., Leipzig (1944).
15. I. M. KOLTHOFF AND H. A. LAITINEN, *Science*, **92**, 152 (1940).

The Reproducibility of the Manganese Dioxide Electrode and the Change of Electrode Potential with *p*H[1]

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ABSTRACT

The reproducibility and constancy of manganese dioxide electrodes with ammonium chloride electrolyte were improved by pretreatment of the dioxide with ammonia, the dioxide used having acid properties. The electrode potential of such electrodes varies not only with *p*H, but also with the concentration of ammonium ion or free ammonia. The apparent change with *p*H when the ammonium chloride concentration is constant is larger than 0.059 *p*H.

INTRODUCTION

There is little information on the conditions necessary for reproducibility of the manganese dioxide electrode in solutions of low acidity. Drucker and Hüttner (1) attempted to compare different manganese oxide preparations by means of electrode potentials, and seem to have regarded 30 to 40 mv as a negligible difference. Cahoon (2) was able to attain averages of four electrodes in the same electrolyte accurate to 5 mv with an African manganese dioxide. Ferrell and Vosburgh (3) found electrolytically prepared electrodes neither very reproducible nor constant in electromotive force, although quite reproducible in discharge characteristics. Jennings and Vosburgh (4) were able to reproduce electrodes of precipitated manganese dioxide in electrolytes of ammonium and zinc chlorides with a maximum variation of 5 mv. At the beginning of the present investigation electrodes made with a different manganese dioxide preparation than used by Jennings and Vosburgh and an electrolyte of higher *p*H were less reproducible than this. Consequently a further study of conditions necessary for reproducibility was undertaken. One cause of variability and inconstancy of electrode potential has been found to be a slow exchange of protons from hydrated manganese dioxide and cations from the electrolyte, with conversion of part of the manganese dioxide to a salt form. When this reaction is brought to an approximate equilibrium by preliminary treatment of the manganese dioxide, electrodes are much more reproducible and more nearly constant than otherwise.

The partial neutralization of the manganese dioxide should have an effect on the change of electromotive force with *p*H. It has been assumed in the past that the variation of the electrode potential, E, with *p*H should be given by the equation

$$E = E^0 - k\text{pH} \qquad \text{(I)}$$

in which E^0 is constant and k is 0.059 volt per unit change in *p*H within the temperature range 22° to 27°C. Some of the more recent experimental results for k have been higher than 0.059. Daniels (5) found 0.075, Thompson (6) 0.07 and 0.10 for natural and artificial manganese dioxide, respectively, and Cahoon (2) 0.0608 at 27.5°C for a West African pyrolusite. McMurdie, Craig, and Vinal (7) found 0.06 for k from *p*H 6 to 10 and a value of 0.12 in more acid solutions. Drotschmann (8) also found a difference between the acid and alkaline ranges with smaller values of k than the above.

If an unknown fraction of the manganese dioxide is hydrated and has weak acid properties, the composition may be represented by the formula $H_2MnO_3 \cdot xMnO_2$, with one of the hydrogen atoms replaceable. The reduction of the corresponding ammonium salt to manganese oxyhydroxide can be represented by

$$NH_4(HMnO_3 \cdot xMnO_2) + (x+1)H^+ + (x+1)e \rightarrow (x+1)\,MnOOH + NH_3 + H_2O$$

and the dependence of the electrode potential on the various activities should be given by

$$E = E^0 + \frac{0.059}{x+1}\log R - 0.059\ p\text{H} - \frac{0.059}{x+1}\log (NH_3) \qquad \text{(II)}$$

in which R represents a ratio of activities of man-

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ganese dioxide and the lower oxide and (NH_3) represents the activity of free ammonia. At constant R the electrode potential should vary not only with the pH but also with the logarithm of the free ammonia activity. The latter at constant ammonium ion concentration must vary with the pH. Therefore, a variation in E of more than 0.059 ΔpH would be expected. The excess variation above 0.059 ΔpH should depend on x which in turn should be characteristic of the particular manganese dioxide. If x should be very large, corresponding to negligible acid property, the variation in E should be 0.059 ΔpH. This theory is independent of what particular lower oxide is assumed as the reaction product, provided the lower oxide does not react appreciably as an acid.

Experimental

The manganese dioxide used in most of the experiments was prepared by reaction of manganese sulfate and potassium permanganate in acid solution (4). A half-mole batch was washed by nine half-liter portions of water. In the last six washings the precipitate was stirred with the wash water on a steam bath for an hour each time before filtering through hardened filter paper. The last wash water was neutral to litmus and gave no test for sulfate ion. After the washing, the manganese dioxide was dried at 100° to 110°C for 48 hours. Analysis by the arsenite method for available oxygen (9) and the method of Lingane and Karplus (10) for total manganese gave the formula $MnO_{1.967}$ and a calculated water content of 9 per cent.

This preparation was used in a few experiments by Jennings and Vosburgh (4) and was designated by them as II-MnO_2. Their similar I-MnO_2 was also used in this investigation. It differed from II-MnO_2 in having been less thoroughly washed, but was washed with an ammoniacal solution before final washing with water.

An artificial pyrolusite was made from purified manganese nitrate by the method described by Kelley and Moore (11). Analysis gave the composition $MnO_{1.988}$, with practically no water.

Electrodes were made as described by Jennings and Vosburgh (4) except that the vessels were of smaller diameter and the electrolyte contained no zinc chloride and had a pH of 7 or above. Essentially, the procedure consisted of a preliminary digestion of the manganese dioxide either with the electrolyte or as otherwise noted, followed by compression of the mixture of manganese dioxide and electrolyte around the platinum wire of the cell vessel with a pressure of about 500 psi. More electrolyte was placed above the manganese dioxide. The electrode potentials were measured at room temperature (21° to 26°C) against a single reference electrode which was moved from one vessel to another. The reference electrode was checked frequently against a saturated calomel electrode, and electrode potentials are expressed as against the saturated calomel electrode. The pH of the electrolyte was measured by means of a glass electrode and should be reliable to ± 0.02 pH.

Results

Ion Exchange Experiments

The electrodes so made with II-MnO_2 were less reproducible and constant than the similar electrodes made with I-MnO_2 by Jennings and Vosburgh. In agreement with the previous work the digestion of the manganese dioxide with the electrolyte was found to be an important part of the process. When this was omitted the potentials were much too high initially, and the electrolytes became lower in pH as the potential decreased. Even with the digestion procedure the electrode potential was too high at first. It decreased over a period of several days before becoming more nearly constant, and the pH of the electrolyte also decreased. The changes were such as might have been caused by an acid impurity in the manganese dioxide which diffused out slowly. However, because of the thorough washing of the manganese dioxide, the presence of enough acid impurity to account for the variation was improbable. Liepatoff (12) has explained the adsorption of salts by manganese dioxide by assuming that the hydrated oxide is a weak acid which can exchange protons for cations from the solution. Experiments showed that the manganese dioxide used in this investigation also behaved as a weak acid.

Half-gram samples of II-MnO_2 were treated with 50-ml portions of solutions in which the sodium hydroxide concentration varied from 0.001 to 0.020N and which contained sodium chloride for prevention of peptization. After 48 hours, during the first half of which the flask was shaken occasionally, 10-ml samples of the supernatant liquid were run into 25-ml portions of 0.01N hydrochloric acid and the excess acid was titrated with 0.01N sodium hydroxide to the methyl red end point. The base consumed, in millimoles per gram of manganese dioxide, was plotted against the mean activity of the sodium and hydroxide ions in the solution at equilibrium to give the upper curve of Fig. 1. A similar series of experiments with I-MnO_2 gave the lower curve. Activity coefficients for sodium hydroxide given by Harned and Owen (13) were used. A few similar experiments with II-MnO_2 in solutions of ammonia and ammonium chloride were made, but the end points of the titrations were less definite and errors

larger. The data are plotted as the short curve of Fig. 1.

The adsorption of sodium hydroxide by manganese dioxide, like that of bivalent cations by iron (III) hydroxide (14), can be considered an ion exchange reaction. Fairly satisfactory results were obtained in the application of a mass action expression. When an adsorption experiment was tried with the pyrolusite described above, no ammonia was consumed, in agreement with the fact that the pyrolusite contained no hydrogen. Manganese oxyhydroxide (prepared by oxidation of Mn^{++} ion by persulfate at *p*H 8 and 70°C) adsorbed one-sixth as much ammonia as the precipitated manganese dioxide. Whatever the structure of the oxyhydroxide, it should be a weaker acid than hydrated manganese dioxide and neutralize less ammonia of a given concentration. The smaller exchange capacity

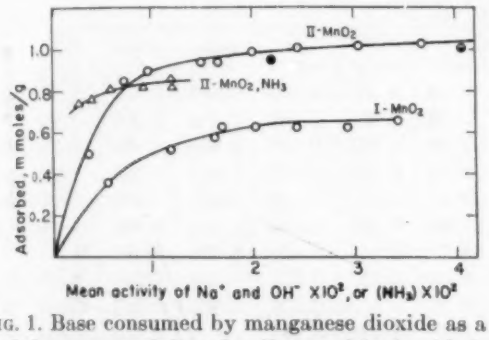

FIG. 1. Base consumed by manganese dioxide as a function of the mean activity of sodium and hydroxide ions, or the ammonia concentration. ○—0.1*M* NaCl; ◒—0.5*M* NaCl; ●—1.0*M* NaCl; and △—0.1*M* NH_4Cl.

of I-MnO_2 can be explained, at least in part, by the treatment with ammonia during the washing process.

The maximum exchange capacity of II-MnO_2 according to Fig. 1 was about 1.05 milliequivalents per gram. From the composition of II-MnO_2, given above, it was calculated that there was 10.2 millimoles of manganese dioxide per gram, and therefore one equivalent of available acid hydrogen to 9.7 moles of manganese dioxide. This suggests a reaction predominately on the surface. Evidence is given later that the exchange was probably incomplete in the time allowed.

Reproducibility of Electrode Potential

On the basis of an ion exchange an explanation can be suggested for the variation of electrode potential and *p*H in new electrodes. When manganese dioxide is packed around an inert electrode, diffusion to and from the main body of the electrolyte is hampered. If complete exchange equilibrium has not been attained previously, the exchange proceeds locally causing a decrease in *p*H within the electrode system, and the electrode potential is higher than corresponds with the *p*H of the outside electrolyte. Diffusion of the acid to the outside electrolyte brings about an increase in the *p*H within the electrode system with decrease of the electrode potential, and then further exchange takes place because it is favored by the higher *p*H. Because of the slowness of diffusion and the possibility of further exchange as diffusion proceeds, slow changes over a period of time may be expected.

This is illustrated in Fig. 2. The curve labelled 1–3 gives the average electrode potential over a four-month period of three electrodes made of II-MnO_2 without digestion with the electrolyte, or other pretreatment. The upper curve, 4–6, is the

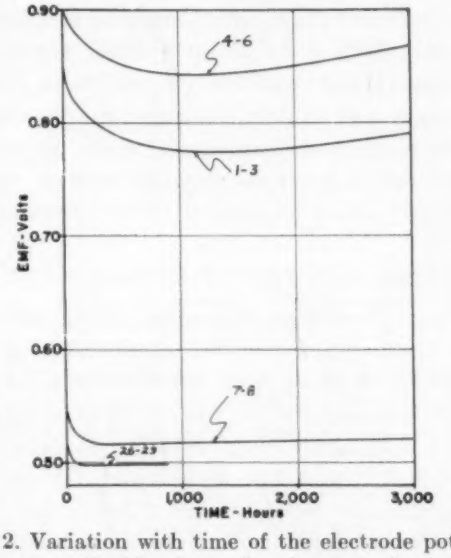

FIG. 2. Variation with time of the electrode potentials of manganese dioxide electrodes (against the saturated calomel electrode) for different treatments of the manganese dioxide.

record of three other electrodes made similarly, but with much less electrolyte; a piece of glass rod replaced most of the electrolyte in the vessel. The electrolyte of both groups was originally at *p*H 7.40, but after 5000 hr the *p*H was 6.65 in the combined electrolyte of cells 1–3 and 2.78 in the much smaller volume of electrolyte in cells 4–6. When manganese dioxide was stirred with some of the electrolyte for 24 hours prior to making the electrodes, the electrode potential was much lower and more nearly constant (curve 7–8), in agreement with previous work (4). Even with this treatment the potential decreased considerably in the early part of the period of observation, and the *p*H after 5000 hours was 6.59 instead of 7.4. The curve labelled 26–29 represents three electrodes made with manganese dioxide previously digested for 24 hours in a solution 1*M* in ammonia and 0.1*M* in ammonium chloride and then washed well with the

electrolyte to be used. These electrodes were the most satisfactory of all with respect to initial change and constancy. They still showed evidence of the release of some acid to the solution, as the *p*H after 1000 hours was 7.18. Experience with a number of similar electrodes showed that the reproducibility was always good. Many groups of four similar electrodes had average deviations in potential of one mv or less for periods of several weeks. In a few cases in which larger differences developed after a time it was found that they could be accounted for largely, at least, by differences in *p*H.

It may be concluded that an important condition for the making of reproducible and constant manganese dioxide electrodes is that the manganese dioxide be brought to exchange equilibrium with the electrolyte. This cannot always be accomplished in reasonable time by simple contact between the manganese dioxide and the electrolyte in the type of electrode used in this investigation. An approach to equilibrium conditions can be made by pretreatment of the manganese dioxide with a solution considerably more alkaline than the electrolyte.

Change of Electrode Potential with pH

The theory represented by equation (II) was tested by the construction and measurement of a series of electrodes in which both the ammonium chloride concentration and the *p*H varied. Electrolytes were prepared with ammonium chloride concentrations of 2.0, 0.5, 0.1, and 0.01 mole/l and, for each ammonium chloride concentration, three or four different ammonia concentrations to give solutions of *p*H 7, 7.5, 8, and 9. Four electrodes were prepared with each of the electrolytes. The manganese dioxide was pretreated by digestion for 24 hours at room temperature in a solution of 1 mole/l of ammonia and 0.1 mole/l of ammonium chloride.

The electrode potentials over a period of 26 weeks are given in Table I. Each value is the average of four potentials with an average deviation in most cases of about one mv. The *p*H values given are those found by measurement of the combined electrolytes of the electrodes in question.

The *p*H values in the table were those determined after the first four weeks for all but the first two groups of cells. The electrolytes of the first two groups at this time had increased in *p*H from initial values of 7.0 and 7.5 to 7.46 and 7.76, respectively. All others had decreased by an average of 0.28 *p*H with only three values outside the range 0.28 ± 0.10. All electrolytes except those of *p*H 8.7 were replaced by fresh electrolytes after the four-week electromotive force measurement and 16 weeks later these were removed and tested, following the 20-week electromotive force measurements. The changes had continued, although the average change calculated for a four-week period was less than before. The change still continued when a second fresh electrolyte was added. These changes suggest that in most of the electrodes complete exchange equilibrium had not been attained in the pretreatment and that the exchange continued at a slow rate for a long time.

Since the measurements in the two last columns were usually not made at the same *p*H as the four-week measurements they were corrected to the same *p*H by the use of data to be given later. Half of the corrections were less than 10 mv and the other half varied from 10 to 45 mv. Because of the corrections these values must be considered less reliable than the others, but only qualitative conclusions are based on them. The data for the first, second, and fourth groups are exceptions, and their slightly different treatment is described below.

TABLE I. *Variation of electrode potential with* pH *and with time*

NH_4Cl *M*	*p*H	Electrode potential, volts					
		Initial	1 week	2 weeks	4 weeks	20 weeks	26 weeks
0.01	7.46	0.503	0.503	0.507	0.510	0.518	0.506
0.01	7.76	0.484	0.483	0.485	0.491	0.498	0.501
0.01	7.88	0.477	0.479	0.480	0.484	0.468	0.472
0.1	6.94	0.527	0.529	0.531	0.535	0.537	0.523
0.1	7.27	0.517	0.518	0.518	0.521	0.500	0.502
0.1	7.66	0.487	0.484	0.484	0.484	0.459	0.465
0.1	8.72	0.444	0.409	0.406	0.402	0.371	0.365
0.5	6.66	0.557	0.557	0.556	0.556	0.523	0.523
0.5	6.90	0.537	0.536	0.536	0.537	0.517	0.512
0.5	7.76	0.489	0.474	—	0.470	0.444	0.448
0.5	8.70	0.449	0.405	0.396	0.392	0.351	0.360
2.0	6.62	0.538	0.534	0.534	0.530	0.510	0.509
2.0	7.18	0.520	0.498	0.497	0.498	0.481	0.473
2.0	7.70	0.481	0.464	0.464	0.463	0.432	0.431
2.0	8.76	0.440	—	0.392	0.380	0.337	0.343

Most of the electrodes were fairly constant in electrode potential during the first four weeks, but decreased between four and 20 weeks. This decrease is discussed later. The best constancy was observed for the solutions of lowest *p*H and for the solutions of higher *p*H when the ammonium chloride concentration was not too high, although as mentioned above, the *p*H changed, indicating continued exchange. There was an indication of excessive pretreatment for the 0.01 mole/l ammonium chloride electrodes, since the electrolytes became more alkaline than originally.

The electrodes of *p*H 8.7 to 8.8 (originally 9) were more variable than any of the others and never came to satisfactory constancy. The data for these electrodes were omitted in the interpretation of the results.

Fig. 3 shows the electrode potentials plotted against the measured *p*H. The potentials plotted were the four-week values (or averages closely agreeing with these) except for the first, second, and fourth groups. Since these increased in electrode potential at first, it was considered that the maximum values were least in error. In each case, the *p*H measured at the time of the accepted electrode potential was used and is the value given in Table I.

The points for each different concentration of ammonium chloride in Fig. 3 lie on a different straight line. This is evidence that the electrode potential is dependent on some other factor than *p*H alone. The average slope of the lines of Fig. 3 is 0.075 volt *p*H unit. The slope of the 2-mole/l line is 0.062, that of the 0.01-mole/l line 0.082, and of the other two 0.077 volt *p*H unit, but reason is given later for thinking that these differences are not significant.

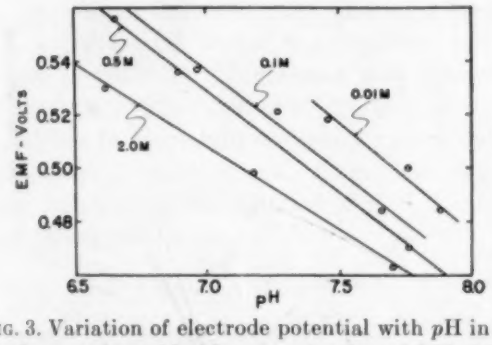

FIG. 3. Variation of electrode potential with *p*H in solutions of ammonium chloride concentration of 0.01, 0.1, 0.5, and 2 mole/l.

From Fig. 3 it may be concluded that the variation with *p*H does not follow equation (I), because not only are the slopes too large, but the electrode potential depends on the ammonium ion concentration (or alternatively on the free ammonia concentration) as well as on the *p*H. These two facts are qualitatively in agreement with equation (II).

Equation (II) can be tested quantitatively by the plotting of $(E + 0.059\ pH)$ against log (NH_3). Then, if R is constant the points should fall on a straight line of slope $0.059/(x + 1)$. Such a plot is shown in Fig. 4. The free ammonia activity (NH_3) was calculated from the acidic dissociation constant of ammonium ion (15). Activity coefficients for ammonium ion in 0.01, 0.1, and 0.5 mole/l ammonium chloride from freezing point measurements (16) were used without correction to 25°C since the change with temperature is small (15). For the 2-mole/l solution the activity coefficient was estimated by extrapolation with the help of the activity coefficients of rubidium and cesium chlorides (17).

Fig. 4 reveals a dependence of the electrode potential on the free ammonia concentration, if the *p*H dependence is assumed to be the theoretical one. The data can be accounted for satisfactorily by equation (II). The experimental points are reasonably close to the line, considering the difficulties. An error of 0.04 *p*H, for example, since it would affect both coordinates, would account for the deviation of many of the points from the line. One point is too far off, and the same point has considerable effect on the slope of the 2-mole/l curve in Fig. 3, making it doubtful whether the differences in slope in Fig. 3 are significant.

From the slope of the line of Fig. 4, which is equal to $0.059/(x + 1)$ according to theory, $(x + 1)$ can be calculated to be 3 moles of manganese dioxide to one mole of ammonium ion. This disagrees with the value of nearly 10 moles found in the exchange experiments for the ratio at the maximum capacity when sodium hydroxide was the base. The ratio was even larger for ammonia. The observation of

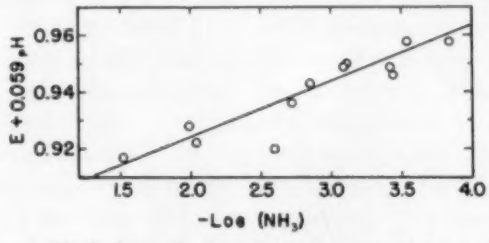

FIG. 4. Variation of the electrode potential with free ammonia activity when the variation with *p*H is assumed to be 0.059 volt per unit *p*H change.

continued exchange mentioned above suggests an explanation. The electrode potential is doubtless determined by the condition of the exterior of the manganese dioxide particles, while the exchange results were calculated on the basis of the composition of the whole particles. The continued slow exchange is evidence that the interior of the particles differs from the exterior.

It has been assumed that R of equation (II) is constant. For large variations in the amount of adsorbed ammonia, corresponding to large *p*H differences, this might not be true. Also, if at a low *p*H an appreciable fraction of the manganese dioxide reduced should go into solution as Mn^{++} ion, an increased *p*H coefficient would be called for (7). In the more acid solutions x should vary.

On the other hand, manganese dioxide preparations having little or no acid property should give electrodes with the theoretical *p*H coefficient. Such a preparation is the pyrolusite described above which, however, gave poorly agreeing electrodes. If the African pyrolusite used by Cahoon (2) had little acid property, his nearly theoretical *p*H coefficient of 0.0605 is understandable. Alternatively, the use of a varying zinc chloride concentration

might have had an effect on the *p*H coefficient, if zinc ion takes part in the ion exchange. The diverse values in the literature for the *p*H coefficient are not necessarily in disagreement, but may have been correct for the manganese dioxide preparations and conditions employed.

Any discussion of this paper will appear in a Discussion Section, to be published in the July 1953 issue of the JOURNAL.

REFERENCES

1. C. DRUCKER AND R. HÜTTNER, *Z. physik. Chem.*, **131**, 237 (1929).
2. N. C. CAHOON, *Trans. Electrochem. Soc.*, **68**, 177 (1935).
3. D. T. FERRELL, JR., AND W. C. VOSBURGH, *J. Electrochem. Soc.*, **98**, 334 (1951).
4. C. W. JENNINGS AND W. C. VOSBURGH, *J. Electrochem. Soc.*, **99**, 309 (1952).
5. F. DANIELS, *Trans. Am. Electrochem. Soc.*, **53**, 45 (1928).
6. B. M. THOMPSON, *Ind. Eng. Chem.*, **20**, 1176 (1928).
7. H. F. MCMURDIE, D. N. CRAIG, AND G. W. VINAL, *Trans. Electrochem. Soc.*, **90**, 523 (1946).
8. C. DROTSCHMANN, *Metall*, **1948**, 37.
9. I. M. KOLTHOFF AND E. B. SANDELL, "Textbook of Quantitative Inorganic Analysis," p. 605, The Macmillan Co., New York (1947).
10. J. J. LINGANE AND R. KARPLUS, *Anal. Chem.*, **18**, 191 (1946).
11. K. K. KELLEY AND G. E. MOORE, *J. Am. Chem. Soc.*, **65**, 782 (1943).
12. S. LIEPATOFF, *Z. anorg. u. allgem. Chem.*, **152**, 73 (1926).
13. H. S. HARNED AND B. B. OWEN, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., p. 369, Reinhold Publishing Co., New York (1950).
14. M. H. KURBATOV, G. B. WOOD, AND J. D. KURBATOV, *J. Chem. Phys.*, **19**, 258 (1951).
15. R. G. BATES AND G. D. PINCHING, *J. Research Nat. Bur. Standards*, **42**, 419 (1949).
16. G. SCATCHARD AND S. S. PRENTISS, *J. Am. Chem. Soc.*, **54**, 2696 (1932).
17. R. A. ROBINSON AND D. A. SINCLAIR, *J. Am. Chem. Soc.*, **56**, 1830 (1934).

High Capacity Magnesium Dry Cells[1]

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ABSTRACT

Magnesium dry cells patterned after the conventional Leclanché cell now appear to be worthy of acceptance in many applications. The cell contains a magnesium alloy anode, $MnO_2 + BaCrO_4$ + acetylene black cathode, magnesium bromide electrolyte inhibited with lithium chromate, and a paper separator. The cell is characterized chiefly by very high capacity, particularly when the load resistance is designed for the voltage level of the cell. In series batteries, the optimum number of cells is 15 to 30 per cent less than the number of Zn cells required for the desired voltage. Cells made during the early stages of development have now been successfully stored two years, retaining more than 85 per cent of their initial capacity. Low temperature discharge properties are highly promising and tropical storage properties are outstanding.

Introduction

Initial work on the development of a Leclanché type magnesium dry cell under sponsorship of the U. S. Army Signal Corps was reported by Kirk and Fry in 1948 (1). Magnesium was selected for this development because of its unique advantages with respect to availability, electrode potential, and electrochemical equivalence. Numerous improvements, particularly in capacity and shelf life, are herein described.

Cell Composition

Typical cell compositions are shown in Table I, with a more detailed description as follows:

Anode.—AZ31A alloy (Mg-3Al-1Zn-0.2Mn-0.15 Ca) has been found to have the best combination of battery anode properties of the many alloys tested. It is easily formed by impact extrusion and has good shelf life and fairly uniform discharge corrosion. The calcium aids in minimizing delayed action.

All can sizes (N to F) have been made by impact extrusion of slugs cut from extruded rod. The can wall thickness varies with the size of the can, the type of test, and the type of jacket or pack construction used. The thicknesses shown in Table I are suitable for moderately heavy drains (8–100 hour rate).

Electrolyte.—Although any of the alkali and alkaline earth bromides may be used successfully as the electrolyte in magnesium dry cells, magnesium bromide is outstanding (Table II). $MgBr_2$ concentrations of 190–250 g/l are optimum, the higher concentration giving slightly more capacity and smoother discharge corrosion of the magnesium.

A chromate inhibitor is required for successful storage, lithium chromate in 0.20 g/l concentration giving optimum performance with respect to shelf corrosion and delayed action. The lowest chromate concentration which will give adequate corrosion protection is preferred, since delayed action increases with increasing chromate concentration.

Cathode.—The conventional manganese dioxide-acetylene black cathode has been modified by addition of 3 per cent barium chromate, capacity increases of 7 to 15 per cent resulting therefrom. The optimum ratio of ore to black is dependent on the type of test, more black being preferred for light drain service than that required for heavy service. The optimum wetness is in turn a function of the ore-black ratio, the wetness increasing with the black content of the mix (Table I).

Synthetic manganese dioxides show no time capacity advantage over African ore in most standard tests, in spite of an appreciably higher voltage level. Such tests, of course, simulate discharge in lamps and tubes which are designed to the voltage characteristics of the zinc cell. Under these conditions, the effect of the increased voltage obtained from synthetic ore is only to deplete the ore at a faster rate because of the increased current drain. If the equipment is redesigned to take full advantage of the higher voltage of the Mg cell (more resistance and lower current drains, but equal wattage), or if the number of cells in series packs is decreased, synthetic ore then may show an appreciable capacity advantage (see Cell Characteristics).

Separators.—Capacity increases of 25–50 per cent are achieved through use of Kraft paper separators in place of cereal gel.

Air depolarization.—The magnesium dry cell is susceptible to air depolarization, and capacity increases of up to 50 per cent are realized by provision of a small vent (0.02–0.07 in. diam) in the top wax.

[1] Manuscript received December 14, 1951. This paper prepared for delivery before the Buffalo Meeting, October 11 to 13, 1950. Investigation performed under sponsorship of U. S. Army Signal Corps.

The maximum effect is obtained when the drain is relatively light, as in the BA-30 and BA-8 tests. The effect, on the other hand, is very slight in the heavy industrial test.

"D" size cells with a 0.02 in. open vent have shown little tendency to dry out in two years' time at 70°F (Table III, Composition No. I), though in general it is preferred that the vent be omitted or that it be sealed until just prior to discharge. Additional capacity is obtained if the can wall is thin enough to allow rupture during discharge, with the resulting additional entrance of air into the cell. In most cases, however, rupture is undesirable, not so much because of leakage, which is rare with magnesium cells, but because of swelling. The most effective use of air depolarization of the Mg cell will require a study of cell design, a field as yet practically unexplored.

Spot welding.—Side wires are successfully attached to magnesium cells for pack assembly by either spot welding or soldering. The former is, in general, preferred because of its simplicity and greater resistance to corrosion under high humidity conditions.

The preferred wire for spot welding is stranded Cu which is coated with Zn, Sn, or solder, although solid uncoated Cu is also satisfactory. Finished cells may be spot-welded without distortion by simple cradling, even with a wall as thin as 0.020 in. as in the "N" size cell.

TABLE I. *Typical cell compositions*

Cell size	Composition number	Anode		$MgBr_2$ conc	Inhibitor	Cathode				Separator	Vent diam
		Alloy	Wall in.			MnO_2	$BaCrO_4$	AB	Wetness		
				g/l	g/l	%	%	%	ml/1000 g		in.
"D"	I	AZ31A	0.075	190	$0.1Li_2CrO_4$	87	3	10	500	paper	0.07
"D"	II	AZ31B	0.050	190	$10(NH_4)_2CrO_4$	90	—	10	360	cereal	0.02†
"D"	III	AZ31A	0.050	190	$1.0Li_2CrO_4$	90	—	10	360	cereal	none
"D"	IV	AZ31A	0.075	250	$0.20Li_2CrO_4$	91	3	6	360*	paper	0.07
"F"	V	AZ31A	0.075	250	$0.20Li_2CrO_4$	91	3	6	360*	paper	0.07
"AA"	VI	AZ31A	0.038	250	$0.20Li_2CrO_4$	94	—	6	300	paper	0.02
"AA"	VII	AZ31A	0.038	250	$0.20Li_2CrO_4$	91	3	6	300*	paper	0.02
"N"	VIII	AZ31A	0.022	250	$0.20Li_2CrO_4$	91	3	6	300*	paper	none
"D-2A"	IX	AZ31A	0.040	250	$0.20Li_2CrO_4$	91	3	6	360	paper	0.07

* 380 ml/1000 g with electrolytic ore.
† Vent hole open during storage.

TABLE II. *Comparison of bromide electrolytes "D" size cells; anodes—AZ31B*; cathodes—90* MnO_2 + *A.B.; separators —cereal gel*

Electrolyte g/l bromide	Inhibitor g/l $(NH_4)_2CrO_4$	Initial BA-30 capacity	12 Months† BA-30 capacity	Capacity maintenance
		days	days	%
190 $MgBr_2$	10.0	33.2	30.7	92.5
300 LiBr (85%)	5.0	26.5	22.3	84.0
300 $CaBr_2 \cdot 2H_2O$	10.0	25.2	18.1	71.8
225 NH_4Br	10.0	24.0	24.6	102.5
300 $SrBr_2 \cdot 6H_2O$	1.5	17.1	16.5	96.5
200 NaBr	10.0	10.5	—	—
300 KBr	2.0	11.9	—	—

* AZ31B: Mg alloy with 3% Al, 1% Zn, 0.2% Mn, and controlled purity.
† Storage temperature: 70°F.

Cell Characteristics

Voltage and Capacity

The most important characteristics of the magnesium cell are its high voltage and flat discharge curve, which result in an efficiency of utilization of the MnO_2 that is in many cases double that obtained with zinc Leclanché cells. This is shown by the discharge curve of Fig. 1 (BA-30) in which Mg cells are compared with standard Zn cells, the depolarizer in each case being African MnO_2. The initial voltage of these cells was lowered from 1.9 to 1.7 prior to discharge by short circuiting for 1.5 minutes. Other typical capacities are shown in Table III.

In adapting the magnesium cell for specific applications, the voltage is one of the most important considerations. This is important not only from the standpoint of lamp and tube life, but also in order that maximum benefit may be derived from the high voltage.

Obviously, the most effective use of the high voltage is made when the load resistance is designed to give the desired wattage at the voltage level of the Mg cell. Therefore, if Mg cells are to be used in place of zinc cells in existing applications, maximum efficiency can be obtained in one of two ways: (*a*) replace the lamps or tubes with others of higher resistance, maintaining the same wattage range (see Fig. 2 and 3); or (*b*) decrease the number of cells in series in pack batteries (Fig. 4).

If the application is such that neither of these

TABLE III. *Capacities of typical magnesium batteries*

Test	Cells			Specification (Zn cells)	Capacity (Mg cells)
	Number	Size	Comp		
BA-30—Init.	1	"D"	I	14 days	37.6 days
BA-30—1 year 70°F	1	"D"	I	12 days	34.3 days
BA-30—Init.	1	"D"	II	14 days	33.3 days
BA-30—2 years 70°F	1	"D"	II	—	28.7 days
BA-30—Init.	1	"D"	III	14 days	28.0 days
BA-30—6 months 113°F	1	"D"	III	9 days*	23.7 days
BA-8—Init. 70°F	1	"D"	I	220 hr	573 hr
BA-8—Init. 20°F	1	"D"	I	0 hr	78 hr
ASA hvy. ind.	1	"D"	IV	750 min	1220 min
ASA RR lantern	3 (series)	"F"	V	45 hr	96 hr
ASA hearing aid "A"	2 (parallel)	"AA"	VI	10 hr	27 hr
ASA hvy. hearing aid "B"	11 (series)	"N"	VIII	400 hr†	456 hr
BA-270 "A"	6 (parallel)	"D-2A"	IX	20 hr	46 hr
BA-270 B_1	60 (series-par.)	"N"	VIII	20 hr	48 hr
BA-270 B_2	30 (series)	"N"	VIII	20 hr	52 hr

* Specification for 3 months at 113°F.
† Basis 15 Zn cells.

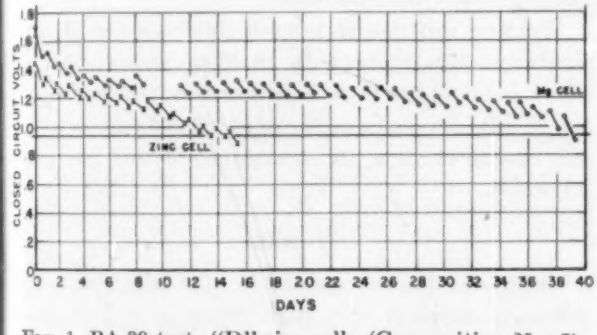

FIG. 1. BA-30 test. "D" size cells (Composition No. I)

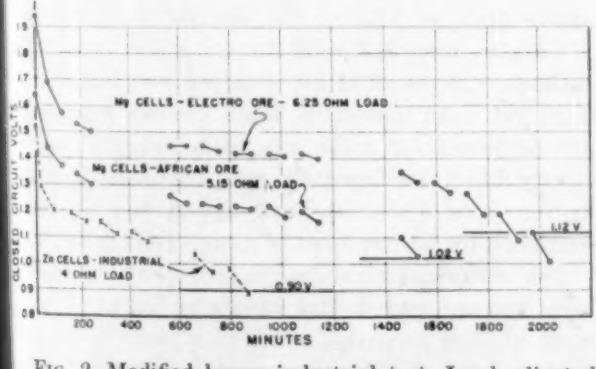

FIG. 2. Modified heavy industrial test. Load adjusted to cell voltage by keeping wattage range same as for zinc cells. "D" size cells (Composition No. IV).

alternatives seems practical, magnesium cells may still be used advantageously with existing equipment in many cases by addition of a dropping resistor. This may be a resistance wire if the construction

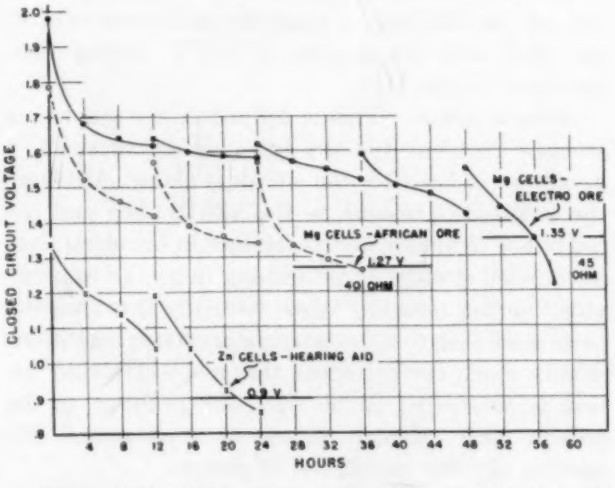

FIG. 3. Modified hearing aid "A" battery test. Load adjusted to cell voltage by keeping wattage range same as for zinc cells. 2 "AA" size cells in parallel (Composition No. VII).

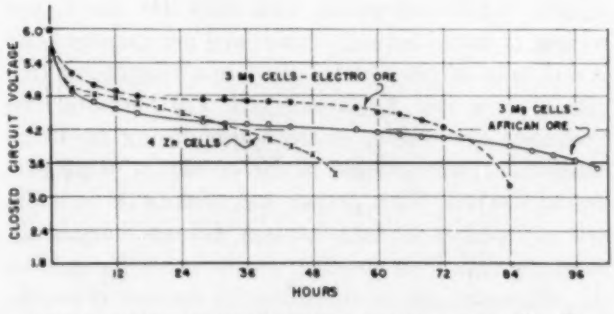

FIG. 4. 32-Ohm railroad lantern test. "F" size cells (Composition No. V).

permits, as in packs, or the internal resistance of the cell may be increased by alteration of the central carbon rod. A dropping resistor usually increases the time capacity to an end voltage through slower utilization of the MnO_2. It has the additional advantages of removing the possibility of overloading the equipment and of decreasing the rate of Mg consumption, thus lessening the possibility of rupture or swelling during discharge.

Low temperature service.—The low temperature discharge characteristics also offer great promise. A BA-8 capacity at minus 20°F of 78 hours, or 14 per cent of the 70°F value, was obtained, though no attempt was made to tailor the cell for low temperature service (Table III).

Shelf life.—Successful two-year storage of $MgBr_2$ cells, with a capacity maintenance of 86 per cent, has been demonstrated (Table III). Numerous batches have had capacity maintenances of more than 90 per cent after one year, and these include paper-lined as well as cereal gel separator cells. Because of the relatively low electrolyte concentration, magnesium cells suffer no appreciable harm from loss of moisture by evaporation during storage.

The tropical storage properties of the magnesium cell are outstanding, a capacity maintenance of 85 per cent after six months at 113°F having been obtained (Table III).

Delayed action.—This is defined as the number of seconds required for the cell voltage to reach a minimum of 1.0 after the circuit is closed. Although the addition of calcium to the AZ31B alloy and the use of low chromate concentrations in the electrolyte have aided greatly in minimizing delay, an appreciable time lag remains. While normally this amounts to no more than 2–3 seconds, under certain conditions it may reach several times this much. Delayed action is considered to be the chief problem at the present time, though in many applications this amount of delay should not be serious.

Anode efficiency.—The electrochemical efficiency of the AZ31B anode is normally about 60 per cent, compared with 90–95 per cent for zinc. However, because of magnesium's extremely low equivalent weight (12.16 compared with 32.7 for zinc), the weight of metal actually consumed per ampere-hour is still only 60 per cent as great in a magnesium dry cell as in a zinc Leclanché cell. Furthermore, the hydrogen gas evolved at the anode during discharge causes no disadvantages in the operation or properties of the cell. With proper wax sealing or with the cell embedded in tar, the gas diffuses harmlessly from the cell. It is possible, on the other hand, that the efficiency can be increased by further research, thus decreasing the metal requirement.

Leakage.—Although the magnesium can may perforate or split during the later stages of discharge if the wall section is thin, leakage is rare. This is due to the hard and dry nature of the $Mg(OH)_2$ corrosion product which forms throughout the cell during discharge.

Discussion

Unlike most high capacity cells, the magnesium dry cell should not be expensive. Items contributing to expected low costs are the suitability of conventional cell designs and inexpensive materials, such as African MnO_2; low metal requirement and ease of metal fabrication; simplicity of the spot-welding process for side wire attachment; and the relatively small number of cells required in series batteries. On an energy cost basis in particular, the outlook is highly favorable.

Although many factors must be considered in the selection of applications for the magnesium cell, early acceptance in several fields appears to be warranted. These, in general, are applications which require a moderately heavy to heavy drain and in which capacity is important. Outstanding examples are the portable radio, hearing aid, and industrial flashlight and lantern fields.

Work is continuing toward improving cells, particularly with respect to delayed action, and an effort is being made to expedite the production and use of Mg dry cells in those applications where the cell characteristics and economic factors are most favorable.

Summary

Numerous improvements in the magnesium dry cell have resulted in a high capacity cell which is ready for acceptance in many applications.

Patterned after the Leclanché cell, the preferred anode alloy is AZ31A, the electrolyte is 190–250 g/l $MgBr_2$ inhibited with 0.2 g/l Li_2CrO_4, and the cathode consists of MnO_2 + 3 per cent $BaCrO_4$ + 6–10 per cent acetylene black. Paper separators are preferred for maximum capacity. The cell is susceptible to air depolarization, particularly in the lighter types of service. Pack construction has been simplified by development of a spot-welding method.

The magnesium cell is characterized chiefly by high voltage and a flat discharge curve, which, when utilized properly, result in capacities that are double those of the corresponding Leclanché cells. Successful 70°F storage of two years with gel separators has been demonstrated, and equally successful storage of paper-lined cells is anticipated on the basis of one year results. The low temperature discharge properties offer great promise, and the tropical storage properties are outstanding. The chief problem at the present time is a delayed action of several

seconds, although this is believed to be acceptable in many applications.

The maximum benefit from the high voltage of the magnesium cell is realized when the load resistance is adjusted to the voltage level of the cell. This may be accomplished by using properly designed lamps and tubes or by decreasing the number of cells in series in pack batteries. A dropping resistor may otherwise be used to lower the voltage to the Zn cell range.

The cost/service ratio is expected to be highly favorable in most applications. The portable radio, hearing aid, and industrial flashlight fields appear most promising for early acceptance. Work is continuing on the development of these applications and on further cell improvements.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1953 issue of the JOURNAL.

REFERENCES

1. R. C. KIRK AND A. B. FRY, *Trans. Electrochem. Soc.* **94**, 277 (1948).

Water-Activated Primary Cells Using Alkali Metal Persulfates As Depolarizers[1]

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ABSTRACT

Alkali metal persulfates may be activated by silver compounds so that they become efficient depolarizers when used in water-activated cells having magnesium anodes and silver cathodes. A water-activated primary cell utilizing this system has been developed which is similar to the silver chloride-magnesium cell but which has a 90 per cent greater ampere hour output per unit of volume. The cathode consists of a silver electrode coated with a depolarizing mixture of silver chloride powder and potassium persulfate. Both the silver chloride and the potassium persulfate are used at high efficiency. The cells may be discharged at heavy drain rates with substantially flat discharge curves at relatively high potentials. Because the relatively low cost potassium persulfate replaces a major portion of the high cost silver chloride of the silver chloride-magnesium cell, the cost of both the cells and the generated electrical energy is decreased.

Introduction

During the last decade a number of new types of primary batteries have been developed as described by Vinal (1). Some of these are of the reserve type which is kept dry until activated at the time of use by admission of the proper electrolyte, after which the cell is discharged completely within a short time. In such reserve cells it is possible to use, at high efficiency, oxidizing materials (depolarizers) which are relatively unstable in the presence of the electrolyte, i.e., after activation. Among the considerable number of oxidizing compounds of this class which are attractive theoretically are the alkali metal persulfates. However, when used in water solutions in primary cells the persulfates do not perform satisfactorily. After it was discovered that the persulfates could be used effectively as depolarizers in the presence of silver or silver compounds, the experimental work described in this paper was undertaken and the conditions established for making a practical cell.[2]

The depolarizing action which results from the reduction of an alkali metal persulfate such as potassium persulfate may be represented as follows:

$$K_2S_2O_8 + 2 \text{ electrons} \rightarrow K_2SO_4 + SO_4^{=}$$

Experimental

The first experiments on which this development is based had for their object the improvement of the silver chloride-magnesium, water-activated cell (2). When potassium persulfate solutions were used as electrolytes (3, 4) in these cells a substantial increase in capacity indicated a depolarizing action by the persulfate. However, the depolarizing action by the persulfate occurred only at the silver chloride-electrolyte boundary. The amount of potassium persulfate that could be furnished to this boundary by means of the electrolyte solution was limited by its low solubility in water (5.3 g/100 ml of water at 20°C). As a result of these observations the cell construction for further experimental work was changed so that the surface of the silver chloride electrode was faced with a coating of bound particles of potassium persulfate or sodium persulfate. Thereby a readily available supply of persulfate was located at the silver chloride electrode surface.

Cell Construction

The experimental cells were made of an anode of unalloyed magnesium in strip form and a cathode of silver foil faced with the depolarizer. When alkali metal persulfate was used either alone or mixed with the silver catalyst, it was applied as a paste to the surface of the silver foil. The depolarizer and anode were separated by a thin layer of absorbent paper. The electrodes, being thin and flexible, were assembled into a cell by rolling the components into a concentric capsule-type cell. The cells were activated by continuous immersion in tap water, usually at 21°C.

The specifications for the first two series of experimental cells follow:

Anode: high purity magnesium strip (unalloyed) 0.006 in. (0.15 mm) x 1⅜ in. (3.5 cm) x 25 in. (63.5 cm)

Cathode: 23 in. (58.4 cm) x 1.35 in. (3.5 cm) x 0.001 in. (0.025 mm) rolled silver foil with an

[1] Manuscript received September 21, 1950. Paper prepared for delivery before the Buffalo Meeting, October 11 to 13, 1950.

[2] I. C. Blake and J. B. Mullen (To Burgess Battery Company), U. S. Pat. 2,534,403, December 19, 1950.

electrodeposited coating of silver chloride electrochemically equivalent to one amp min/in.² (0.155 amp min/cm²) of foil surface. A paste of persulfate containing a binder of polyvinyl acetate dissolved in ethyl acetate was applied to the silver chloride layer.

Separator: one thickness of absorbent paper $1\frac{5}{8}$ in. (4.1 cm) wide and 0.005 in. (0.13 mm) thick.

Construction: the elements were rolled into a capsule-type cell.

This particular size of silver chloride-magnesium cell (without the persulfate) is designated by the factory as a 1CC40 cell. For convenience, this construction will hereinafter be referred to as the 1CC40 cell.

Persulfate Coating Without Admixed Silver

In the first series, three groups of cells were made in which 10 g of potassium persulfate, 10 g of sodium persulfate, and no persulfate (control), respectively, were applied to the silver chloride electrode of the 1CC40 cells. These cells were activated by continuous immersion in tap water at 21°C while discharging through a resistance of 3 ohms continuously to an end point of 1.00 v per cell. The average discharge curves are shown in Fig. 1. These show that the cells containing persulfate discharge at a high potential for a much longer time than do the controls, the discharge curve being nearly flat at this high potential.

In the above tests the electrochemical efficiency of persulfate usage was 19.8 per cent for potassium persulfate and 33.3 per cent for sodium persulfate. These efficiency values were calculated by subtracting the electrochemical equivalent of the silver chloride in the cell in amp min from the total output of the cell above 1.00 v in amp min and then determining the ratio between this value and the value obtained by multiplying the number of grams of potassium persulfate by 11.90 amp min or the number of grams of sodium persulfate by 13.50 amp min. The greater efficiency of the sodium persulfate is due to its greater solubility in water.

It is obvious that the addition of the solid persulfate increases the cell volume of the 1CC40 silver chloride-magnesium cell which has a capacity of 1 amp hr/in.³ (0.061 amp hr/cm³) of cell volume under the conditions of discharge outlined above. To determine the effect on cell discharge efficiency (on a volume basis) caused by the addition of the solid persulfate, cells were made in which potassium and sodium persulfates were coated onto the silver chloride electrodes of the 1CC40 cells in amounts ranging from 0.161 to 0.568 g/in.² (0.025 to 0.088 g/cm²) of electrode area. These cells were activated and discharged as described. The cell volume efficiency was increased by sodium persulfate up to an optimum quantity of 0.245 g added/in.² (0.038 g/cm²) of cathode area or 15 g/cell. With this optimum addition of sodium persulfate, the cell capacity was increased from 1 amp hr/in.³ (0.061 amp hr/cm³) to 1.28 amp hr/in.³ (0.078 amp hr/cm³) of cell volume. By the addition of potassium persulfate the cell volume efficiency increased with additional persulfate up to an optimum of 0.484 g/in.² (0.075 g/cm²) of cathode area or 14.8 g/cell. The cell capacity per cubic in. was 0.86 amp-hr (0.052 amp-hr/cm³) with the optimum addition of potassium persulfate.

The above group of experiments showed that, for any given addition of persulfate to the 1CC40 cell, the sodium salt was more efficient electrochemically than the potassium salt.

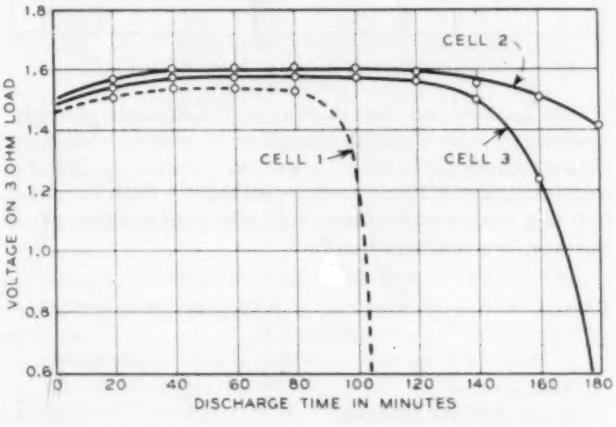

FIG. 1. Discharge curves showing effect of adding sodium and potassium persulfates to type 1CC40 cells, cathodes coated with persulfate. Cell 1—conventional 1CC40 cell; cell 2—1CC40 cell + 10 g sodium persulfate; cell 3—1CC40 cell + 10 g potassium persulfate.

A second series of cells of the 1CC40 type was then made in which the persulfate was coated directly onto the silver electrode in the absence of silver chloride. Fifteen grams of sodium persulfate mixed with binder were pasted onto the silver foil surface to serve as the only depolarizer. These cells were discharged under the previously described conditions along with similar cells in which the silver chloride coating on the silver electrode had not been omitted, together with another group in which the persulfate was entirely omitted (control). Average discharge curves for these three test groups are shown in Fig. 2.

The data in Fig. 2 show that the capacity of cell 3 (using persulfate and silver chloride as depolarizer) is greater than the capacities of cell 1 (using silver chloride in the same amount as cell 3 as depolarizer) and cell 2 (using persulfate in the same amount as cell 3) combined. The fact that these capacities are

not additive suggests that when a persulfate and silver chloride are used in combination in a cell some reaction occurs that does not occur when either material is used alone.

An investigation of the relative costs of sodium persulfate and potassium persulfate revealed that the cost of the sodium salt was approximately twenty times as great as the cost of the potassium salt. Potassium persulfate was therefore used in the experiments described in subsequent parts of this paper because one object of the investigation was the development of a practical reserve type cell.

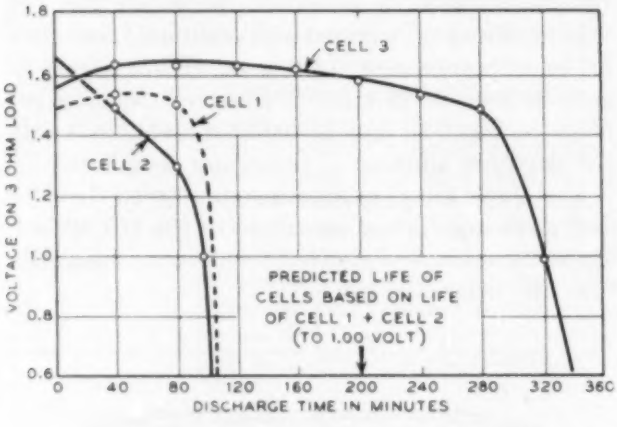

FIG. 2. Discharge curves of type 1CC40 silver chloride-magnesium cells showing the effect of coating the silver chloride-silver cathode with sodium persulfate. Cell 1—conventional 1CC40 cell; cell 2—cathode of 0.001 in. silver foil, 15 g sodium persulfate; cell 3—cathode of silver-silver chloride, 15 g sodium persulfate.

Depolarizer Mix of Powdered Silver Chloride and Persulfate

The data of Fig. 2 suggested the use of a depolarizer consisting of an intimate mixture of potassium persulfate and powdered silver chloride. Three groups of test cells constituting the third series and having the following general specifications were then made:

Anode: high purity unalloyed magnesium strip 0.006 in. (0.15 mm) x 1.35 in. (3.5 cm) x 12 in (30.5 cm)

Cathode: silver foil 0.001 in. (0.025 mm) x 1.35 in. (3.5 cm) x 10 in. (25.4 cm)

Persulfate: 6.50 g of $K_2S_2O_8$ mixed to a paste with a binder of polyvinyl acetate dissolved in ethyl acetate.

Separator: absorbent paper 0.005 in. (0.13 mm) thick x $1\frac{5}{8}$ in. (4.1 cm) wide.

Construction: spirally-rolled cell.

In test group A, in Table I, the depolarizer consisted of 3.32 g of powdered electrolytic silver chloride intimately mixed with the potassium persulfate. In test group B, 3.32 g of Mallinckrodt's C.P. silver chloride powder were used in place of the electrolytic product. Control test group C consisted of standard 1CC40 silver chloride-magnesium cells. The cells of these three test groups were activated by continuous immersion in 44 ml of tap water and simultaneously were discharged continuously through a resistance of 7.5 ohms to an end point of 1.00 v/cell. The average performance data are given

TABLE I. *Use of mixtures of 3.32 g of powdered silver chloride and 6.50 g of potassium persulfate as depolarizers in silver-magnesium cells*

1. Test group	A	B	C (control)
2. Type of silver chloride	Electrolytic powder	Chemical powder	Electrolytic sheet
3. Maximum closed-circuit voltage	1.63 v	1.58 v	1.61 v
4. Life to 1.00 v/cell	400 min	500 min	210 min
5. Average voltage to 1.00 v/cell	1.44 v	1.50 v	1.58 v
6. Average current to 1.00 v/cell	0.192 amp	0.200 amp	0.210 amp
7. Amp-hr capacity to 1.00 v/cell	1.28	1.67	0.74
8. Cell volume ($in.^3$)	1.12	0.98	0.84
9. Cell volume ($cm.^3$)	18.4	16.1	13.8
10. Amp hr/$in.^3$ to 1.00 v/cell	1.14	1.71	0.88
11. Amp hr/cm^3 to 1.00 v/cell	0.070	0.104	0.054
12. Electrochemical equivalent of silver chloride in cell in amp-hr	0.58	0.58	1.00
13. Electrochemical equivalent of potassium persulfate in cell in amp-hr	1.29	1.29	—
14. Total electrochemical equivalent of cell depolarizers in amp-hr	1.87	1.87	1.00
15. Capacity in amp-hr due to $K_2S_2O_8$ (assuming 100% efficiency of AgCl reduction)	0.70	1.09	—
16. Efficiency of $K_2S_2O_8$ usage in cell, per cent	54.2	84.4	

in Table I. The cells containing a mixture of chemically precipitated silver chloride powder and potassium persulfate gave an output per unit of cell volume that was 1.92 times greater than the output of the control cells using silver chloride alone.

The Mallinckrodt chemically precipitated C.P. silver chloride powder gave a superior performance to that of the powder prepared by milling electrolytically-formed silver chloride sheet. This superiority is probably due to the much smaller size of the particle.

Alternate Cathode Materials

Although electrode materials other than silver foil were tested with the silver chloride-persulfate depolarizers, silver foil proved to be the most suitable. Carbon-coated copper and carbon-coated glass cloth gave somewhat poorer results followed by copper foil, lead foil, and palladium foil.

The silver chloride in the silver chloride-persulfate depolarizing mixture can be replaced by other insoluble silver compounds with good results. Silver bromide and silver oxide give cells with satisfactory capacities but the operating voltage is lower than with silver chloride. Incomplete experimental work indicates that the action of soluble silver salts, such as silver nitrate or silver sulfate, is similar to that of the insoluble salts.

Of the conductive cathode electrodes tried, silver metal alone appears to catalyze the decomposition of persulfates. Cells were made using carbon strips as cathodes and potassium persulfate as the only depolarizer. These cells gave much lower potentials and capacities than cells using silver foil cathodes and potassium persulfate as the only depolarizer.

Discussion

Fig. 2 shows that in a cell in which sodium persulfate is used in conjunction with silver chloride as the depolarizer, the capacity is much greater than the combined capacities of separate cells using silver chloride and sodium persulfate respectively as depolarizers. Inasmuch as the results are not additive, it is evident that, when sodium persulfate and silver chloride are used together as the depolarizer, there is some reaction that does not occur when either compound is used alone as depolarizer for cells with silver and magnesium electrodes. Vallance, Twiss, and Russell (5) suggest that the increased oxidizing activity of the alkali perdisulfates in the presence of silver salts is due to the instability of silver perdisulfate. Mellor (6) states that the presence of silver ions causes a catalytic decomposition of persulfates. These references therefore suggest that the silver chloride has a catalytic effect on the persulfate.

The data presented in Table I show that much better capacities per unit of cell volume can be obtained by using mixtures of powdered silver chloride and potassium persulfate as depolarizer than with the electrolytic silver chloride sheet. The capacity per unit volume of the cells of group B is 92.5 per cent greater than that of the cells of control group C. The capacity per unit volume of a cell using a mixture of powdered silver chloride and potassium persulfate as depolarizer is much greater than that of a cell in which the potassium persulfate is coated over the surface of a silver chloride sheet electrolytically formed on silver foil. In the experiment in which the optimum amount of potassium persulfate to be added to the surface of an electrolytic silver chloride sheet cathode was determined, it was found that with the optimum addition the cell capacity was 0.86 amp hr/in.^{3} of volume (0.052 amp hr/cm).^{3}

TABLE II. *Comparison of performance of silver-silver chloride-potassium persulfate-magnesium water-activated cells and "D" size flashlight cells*

1. Cell	Water-activated	Dry cell
2. Volume	0.98 in.^{3} or 16.1 cm^3	2.83 in.^{3} or 46.0 cm^3
3. Average discharge current	0.200 amp	0.240 amp
4. Average discharge current density	0.204 amp/in.^{3} or 0.0124 amp/cc	0.085 amp/in.^{3} or 0.0052 amp/cc
5. End point	1.00 v	0.75 v
6. Life in minutes	500	375
7. Capacity in amp-hr to end point	1.67	1.50
8. Amp-hr/in.^{3}	1.71	0.53
9. Amp-hr/cm^3	0.104	0.033

Capacities of silver-magnesium water-activated cells using mixtures of powdered silver chloride and persulfate as the depolarizer are not greatly affected by the current density of discharge within the current density range of 0.20 to 1.50 amp/in.^{3} (0.012–0.092 amp/cm^3) of cell volume. These current density values correspond to currents of from 0.55 to 4.25 amp for a "D" size dry cell on continuous discharge.

In cells using a mixture of silver chloride and alkali metal persulfate as depolarizer, the silver chloride by itself is a good depolarizing agent. Through the use of a persulfate catalyzed by the silver chloride as an auxiliary depolarizer, a cell with improved volumetric efficiency is obtained. The use of persulfate as part of the depolarizer makes possible a cell which has the desirable characteristics of the silver chloride-magnesium cell at a reduced cost of depolarizing materials.

The best cells described in this paper gave capaci-

ties of 1.71 amp-hr/in.^{3} (0.104 amp hr/cm^3) of cell volume. This value may be compared to the capacity of a "D" size dry cell used for flashlight service. It is difficult to make a direct comparison between these water-activated cells and dry cells because the designed rates of discharge and the end points differ greatly. The best comparison of the two types of cells would be one comparing the cells of group B in Table I with a "D" size flashlight dry cell discharged through 4 ohms continuously to an end point of 0.75 v per cell. This comparison is given in Table II. This comparison can be summarized by stating that the best water-activated cells described in this paper deliver three times as much capacity per unit of volume to an end point of 1.00 v per cell as a dry cell of the same size can deliver to an end point of 0.75 v, although the latter is discharged at less than half the current drain.

Conclusions

1. Alkali metal persulfates can be used efficiently as depolarizers in water-activated primary batteries containing magnesium anodes, provided the persulfates are used in close association with silver or a silver salt.

2. A modification of the silver chloride-magnesium, water-activated primary battery has been developed which uses as depolarizer an alkali metal persulfate catalyzed by silver or a silver compound. The modified cell, when discharged, gives the same desirable flat discharge curve that is characteristic of the silver chloride-magnesium battery and has a higher energy output per unit of volume.

3. Sodium persulfate appears to be more efficient as a depolarizer in conjunction with silver or silver compounds than potassium persulfate. From a commercial standpoint, however, the potassium persulfate is the more suitable because of the high cost of sodium persulfate.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1953 issue of the Journal.

REFERENCES

1. G. W. Vinal, "Primary Batteries," John Wiley & Sons, Inc., New York (1950).
2. J. B. Mullen and P. L. Howard, *Trans. Electrochem. Soc.*, **90**, 529 (1946).
3. R. Fichter, *Chimia* (*Switz.*), **1**, 141 (1947).
4. Aluminum-Industrie, A.-G., Swiss Pat. 245,180 (1947).
5. R. P. Vallance, D. F. Twiss, and A. R. Russell, "Textbook of Inorganic Chemistry," p. 184, Chas. Griffen & Co., Ltd., London (1931).
6. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," **10**, 469, Longmans, Green & Co., London (1930).

A High Voltage Pile of the Zamboni Type[1]

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ABSTRACT

A new type of Zamboni pile has been developed made up of cells consisting of a MnO_2-carbon black cathode, aluminum anode, an electrolyte of 0.25 per cent $AlCl_3$, mixed with either a 5 per cent methylcellulose-water solution or a 3.7 per cent gelatin 40 to 50 per cent ethylene glycol-water solution and a fibrous paper. Results indicate suitable performance at temperatures ranging from −30° to +45°C and at currents of 10^{-6} to 10^{-12} amperes.

INTRODUCTION

Although the dry pile is generally attributed to Zamboni who described it in 1812 (2) there are earlier references in the literature (1). Desormes and Hachette in 1803 presented a memoir entitled "Investigations of the Electric Pile of Volta." In 1809 Hachette described his work with a dry pile containing starch.

In 1812 Zamboni (2) described a dry form of voltaic pile containing a large number of disks of a "gold or silver paper" coated on the other side with manganese dioxide. When these disks are stacked one on the other they make a high voltage pile. The electrolyte is actually the salts present in the battery dissolved to some extent in the moisture absorbed from the air. The amount of current which may be drawn from the pile is infinitesimal.

M. de Hue (3) made a pile containing disks of Dutch gilt paper alternated with disks of laminated zinc either as foil or as zinc powder glued to the paper.

In 1840 a pile was constructed at the Clarendon Laboratory (4), Oxford University, which has continued from then until the present to operate a pith-ball pendulum, suspended by a silken thread. The pendulum swings between the two electrified terminal plates of the battery, which act as two plates of a condenser, thus being alternately attracted and repelled as it makes contact with each terminal plate.

For over a century the Zamboni type pile was little more than a scientific curiosity. The first attempt to use this type of pile was made by the British during World War II. After experimental investigations small production quantities of piles of 400–600 v were made for use in an infrared telescope as described by Pratt (5). The structural details of this pile were described by Elliott (6). A mixture of 150 g manganese dioxide, 25 g gelatin, 13 ml of a 10 per cent zinc chloride solution and 700 ml of water was painted on one side of a special paper and after being dried the coated paper was laminated under pressure with tinfoil.

[1] Manuscript received March 17, 1952.

Haberer (4*c*) in this country made a pile of disks coated on one side with zinc dust and on the other side with manganese dioxide. The intercell connections were made with a paraffin paper coated on both sides with graphite.

As outlined above, a number of piles were made by the British which gave a voltage of 0.9 v/cell when fresh but after a few months aging stabilized at 0.7 v. Under a current of 10^{-9} amp, the voltage would drop steadily to about 45 per cent of the initial open-circuit voltage. The practical application of these cells was limited owing to the high internal resistance of the cells which amounted to about 20 megohms per cell.

There are a number of applications today where piles of the Zamboni type would be of importance, especially for high-voltage applications requiring currents of 10^{-6} to 10^{-10} amp over wide temperature ranges. Accordingly, it was deemed advisable to ascertain if piles could be constructed with characteristics even better than those of the British type pile.

This investigation consisted of four phases: (*a*) construction and determination of the characteristics of British Zamboni piles, (*b*) studies of various anodes in the British type of Zamboni piles, (*c*) use of best anodes to study various types of manganese dioxides, electrolytes, papers, and binders for use in piles, and (*d*) construction of new types. This paper gives some results of these studies.

EXPERIMENTAL

Special electrical instruments for measuring the voltage of single cells and high-voltage piles were required because of the high internal resistance of the cells. Special vibrating reed electrometers, modified to measure the voltages, were used. These had a range from 1 to 1000 millivolts so a counter emf was used in the grid circuit of one instrument and the null point potentiometer method was used with another instrument. In either case, a voltage of 2 to 3 v could be measured. For piles of high voltage,

electrostatic voltmeters of 10^{12} ohms leakage resistance were used to measure the voltage.

For discharges of 10^{-6} to 10^{-9} amp, a series of special resistances of 10^{12} to 10^{6} ohms were obtained. These resistances were mounted either in glass or in ceramic so as to maintain the proper resistance. Any moisture or salt from moist hands would vary the resistance of the 10^{12} to 10^{8} resistors so every precaution was necessarily taken to eliminate this effect.

Storage equipment was assembled for both accelerated and normal shelf-life conditions. Various desiccators containing either saturated water vapor, or 10 per cent zinc chloride solution, or calcium chloride, or no humidifying agents were used to store a few cells and batteries made from the various types of materials and mixtures studied.

In attempts to improve the British pile the following components were investigated:

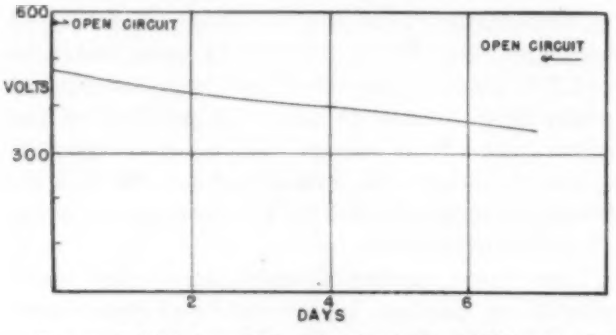

FIG. 1. British type 575 v Zamboni pile of 800 cells, 1.9 cm diam. Discharged at an initial current of 0.035 ma (10^{11} ohm load).

1. Manganese dioxide—a natural ore, one electrolytic and six chemically prepared manganese dioxides.
2. Negative metals—magnesium, aluminum, zinc, tin, silver, gold, and other metals.
3. Electrolyte—water with various percentages of the chloride salt of the metal used as negative.
4. Carbon black—both with the manganese dioxide and as a protective conductive coating for intercell connection.
5. Binding agents—methylcellulose, carboxymethylcellulose, gelatin, casein glue, and albumen.
6. Paper—various grades of bond, alpha cellulose base, hemp fiber base, viscose treated paper, cellophane, parchment, glassine, and various-sized condenser papers.
7. Moisture-proof conducting coating for intercell connection.

Various combinations of these materials have been used in construction of cells and tested both initially and after long storage periods. The combination which best met the requirements was:

(*a*) Manganese dioxide coating: chemically prepared manganese dioxide is sifted through a 200-mesh sieve; 90 per cent of this 200-mesh oxide and 10 per cent carbon black (by weight) is mixed to a paint consistency with an electrolyte consisting of either of two types. One is a low temperature electrolyte composed of a mixture of 0.25 per cent $AlCl_3$, 3.7 per cent gelatin in a 40 to 50 per cent ethylene glycol-water solution. The resulting mixture is kept at 40° to 50°C while it is painted on the paper. The other is a mixture of .25 per cent $AlCl_3$ and a 5 per cent methylcellulose-water solution for normal temperature operation.

(*b*) A Visking fibrous casing is used as the separator for painting with the manganese dioxide.

(*c*) Aluminum is used as the negative. This is molecularly diffused on the separator after the manganese dioxide coating has dried. The process involves placing the MnO_2 coated paper in a vacuum chamber where it is evacuated to .2μ, followed by the evaporation of an opaque aluminum coating from an aluminum covered filament which is electrically heated to the vaporization temperature of the aluminum.

(*d*) The finished sheets of the final product are stored in 21°C temperature and 50 to 60 per cent relative humidity until they are cut into cells for assembly into batteries.

(*e*) The moisture-proof conducting coating is composed of a mixture of 1.5 g of acetylene black and 7.0 g of ethyl methacrylate and vinylite resin mixture. This is thinned to a paint consistency with methyl isobutyl ketone.

Discussion of Results

Fig. 1 shows the performance of the British type pile under a fixed load to give an initial current of 0.035 microamperes. There is an immediate 100-v drop in voltage when the load is applied and after the 7-day test the open-circuit voltage does not return to the original value.

For a comparison with the British cell the preliminary cells developed in this investigation were discharged in a series of individual cell tests at loads of 2.2×10^{7} and 10^{6} ohms. Fig. 2 shows the characteristics of cells with magnesium, aluminum, and zinc negatives as compared with the British cell when subjected to a load of 2.2×10^{7} ohms. Cells with magnesium and aluminum anodes were discharged for 30 days while the British cells lasted for only one day. Similarly Fig. 3 shows the effect of discharges on loads of 10^{6} ohms. These results indicated that changes in composition would improve the performance of the Zamboni type of cell over that of the British.

In order to improve the performance of the Zam-

boni type of cell several modifications were considered essential. First the MnO_2 must be made more conducting so as to furnish a better intercell connection. Secondly, a more conductive electrolyte must be used which is capable of operation over a wide range of temperatures and capable of maintaining its moisture content. Thirdly, the paper used as the base for the coating must be of such a texture that no MnO_2 will penetrate the paper to cause an

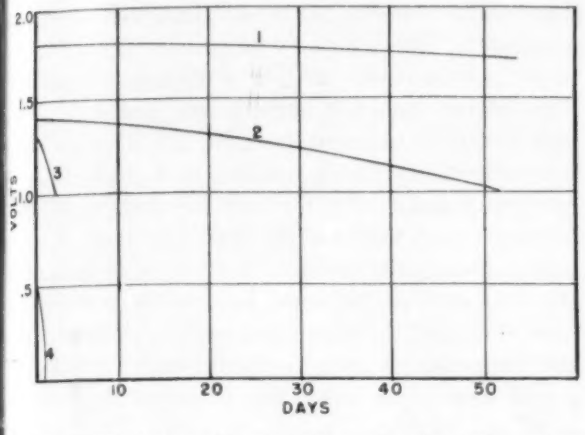

FIG. 2. Discharge characteristics of cells with various anodes under a load of 2.2 x 10^7 ohms. (1) Magnesium negative, (2) aluminum negative, (3) zinc negative, (4) British cell with tin anodes for comparison.

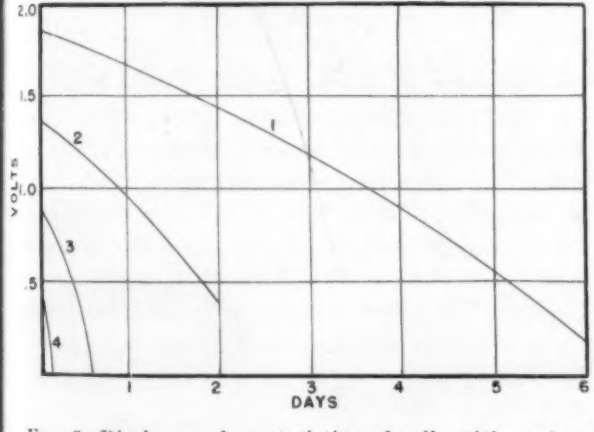

FIG. 3. Discharge characteristics of cells with various metal anodes under a load of 10^6 ohms. (1) Magnesium negative, (2) aluminum negative, (3) zinc negative, (4) British cell with tin anodes for comparison.

internal short with the metal negative. Fourthly, a tight metal-to-paper contact must be maintained so there is a continuous electrolyte path between the MnO_2 and metal negative. Finally, the intercell connection must be conducting and waterproof so that no shorting will take place between the moist MnO_2 coating and the metal negative.

These objectives have been accomplished in the cell described above. The MnO_2 mixed with carbon black has resulted in a much lower intercell resistance. The ethylene glycol-water solution with $AlCl_3$ absorbed in the viscose-impregnated paper tends to stabilize performance over the temperature ranges of $-30°$ to $+45°C$ and at various discharge rates. The molecularly diffused aluminum produces a metal-to-paper bond which will not become defective even under high humidity conditions. The use of a

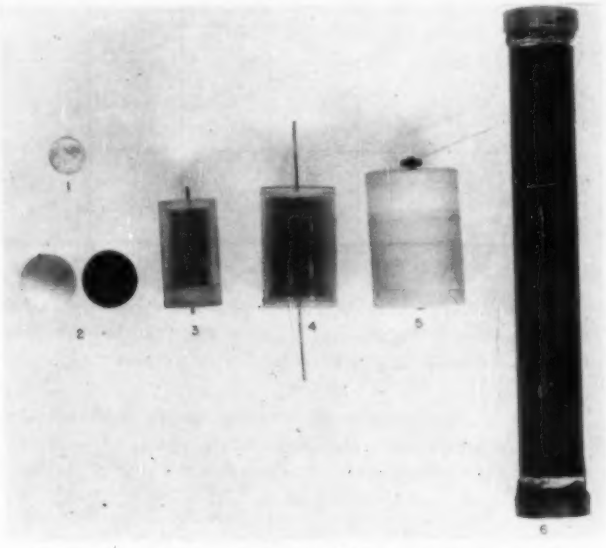

FIG. 4. (1) 1.27-cm diam cell, (2) 1.9-cm diam cells showing aluminum side (left) and MnO_2 side (right), (3) 1.27-cm diam cell battery, 150 v, (4) 1.9-cm diam cell battery, 150 v, (5) 1.9-cm diam cells in special plastic case for 100-v unit, (6) standard 800-cell British made Zamboni pile, 1.9-cm diam cells with a voltage of 5.75 v.

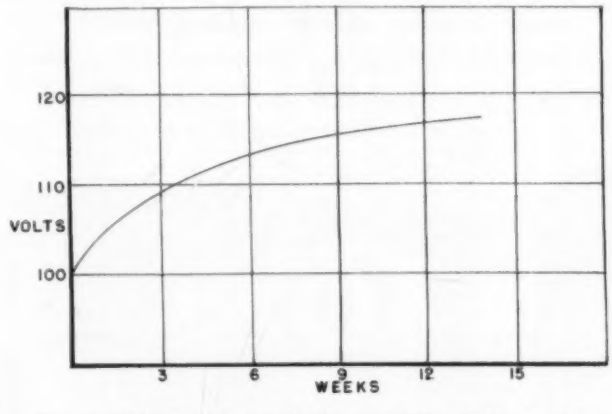

FIG. 5. Voltage characteristics of a 138-v battery of 1.9-cm diam cells using methylcellulose electrolyte. Continuously connected across a 0.035 μf plastic condenser in series with 10^9 ohm resistor.

vinyl-methacrylate lacquer mixed with acetylene black to protect the aluminum surface from moisture at the MnO_2 intercell junction gives a very low resistance intercell connection. The cells must be cut with a self-sharpening die so there is no pull over of material or rough cut edges of the paper. The cells are assembled immediately in the plastic container, placed under a spring pressure of 2 to 3 psi and

sealed. It is important that the pressure is not excessive since this causes the edges to overlap and short-circuit the cells.

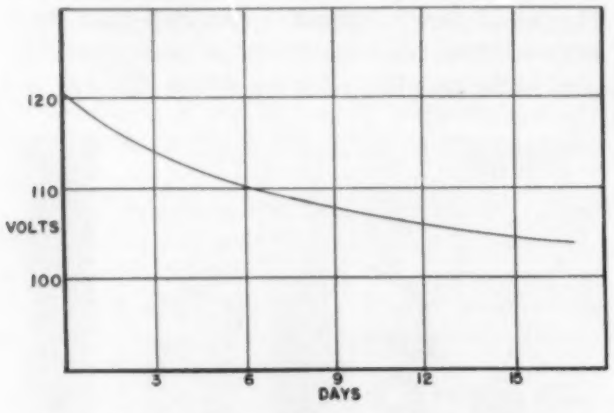

FIG. 6. Voltage characteristics of a 138-v battery of 1.9-cm diam cells using methylcellulose electrolyte. Continuously connected in series with 9 x 10^7 ohm resistor.

TABLE I. *Performance of batteries made with ethylene glycol electrolyte over the temperature range of +20° to −30°C at various currents expressed in per cent of initial voltage at 20°C*

Temp	Initial current drain		
	10^{-9} amp	10^{-10} amp	10^{-11} amp
°C			
+20	100	100	100
+4	88	98	99
−18	48	94	98
−30	28	88	97

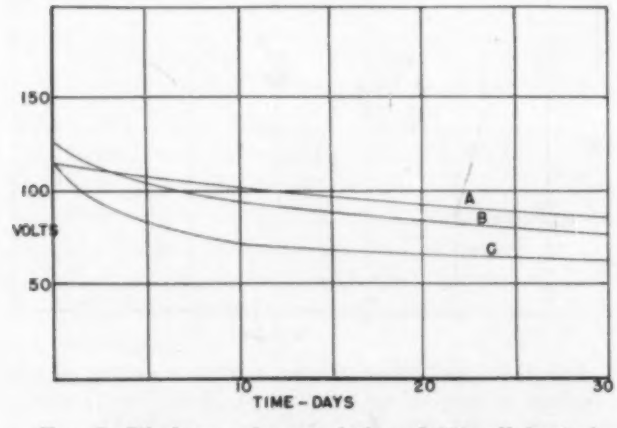

FIG. 7. Discharge characteristics of 100-cell batteries under continuous drain of: (A) Resistance of 1 x 10^{12} ohms, (B) resistance of 1.3 x 10^{11} ohms, (C) resistance of 3.6 x 10^{10} ohms.

Two different sizes of cells have been made for test purposes. These are 1.27 cm (.5 in.) and 1.905 cm (.75 in.) in diameter. The cell thickness ranges from .17 to .25 mm. Fig. 4 shows the appearance of the cells and assembled batteries used in various tests along with the standard British pile. The British cells are about .1-mm thick.

The present design of cell gives 150 v for 2.54 cm (1 in.) length of stack as compared to 110 v for the same length of the British type cells. It is important that the material used to house the pile be of high electrical resistance and low moisture adsorption. Plastics which gave a discontinuous moisture film when wet were used.

Fig. 5 shows the average result of two tests over a period of 14 weeks on the standard methylcellulose electrolyte 138-v battery connected to a .035-μf condenser in series with a 1000-megohm resistor. This battery was not hermetically sealed so it was able to absorb moisture from the air. This increased its conductivity which resulted in a gradual rise in the load voltage. Fig. 6 shows the same type 138-v battery connected to a .035 mfd condenser in series with a 90-megohm resistor for 17 days. In both cases the tests were discontinued because the performance more than met the time requirements. Table I shows the performance of piles made with the ethylene glycol electrolyte over the temperature range of +20° to −30°C.

Fig. 7 gives the performance of batteries made with the ethylene glycol electrolyte under a fixed resistance load for a 30-day period. The actual initial current ranges from 11.4 x 10^{-10} to 1 x 10^{-8}.

CONCLUSIONS

The results of this investigation have shown that an MnO_2-aluminum couple using either $AlCl_3$-methylcellulose-water or $AlCl_3$-gelatin-ethylene glycol-water electrolyte gives satisfactory piles of the Zamboni type. Both give the desired performance for various current drains and the latter electrolyte also gives good performance at low temperature. Shelf-life tests show that molecularly diffused aluminum is durable and that cells have been constructed that give at least a year to 18 months satisfactory shelf life to date.

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Any discussion of this paper will appear in a Discussion Section, to be published in the June 1953 issue of the JOURNAL.

REFERENCES

1. J. L. GAY-LUSSAC, "Sur Les Piles seches voltaiques," *Ann. chim. et phys.*, **11**, 76 (1816).
2. G. ZAMBONI, *Giorn. fis. Chim. Stor. Nat.*, **5**, 424 (1812); **7**, 220 (1814); **9**, 289 (1816).

GILBERT'S *Ann. Physik.*, **51**, 182 (1815); **54**, 1 (1816); **60**, 151 (1819). *Edinburgh Phil. J.*, **1**, 388 (1819).
C. E. BENHAM, "The Dry Pile," Marshall, London.
F. ANERTACH, "Handbuch der Physik," 2nd ed., Vol. 4, p. 185, Barth, Leipsig (1905).
L. GREETZ, "Handbuch der Elektrizitat und der Magnetisms," Vol. 1, p. 441, Barth, Leipsig (1918).
P. F. MOTTELAY, "A Bibliographical History of Electricity and Magnetism," Chas. Griffin & Co., London (1922).
3. WILLIAM HENRY, "Elements of Experimental Chemistry," Vol. 1, p. 163, Robert Desilver, Philadelphia (1819).
4. (*a*) S. P. THOMPSON, "Elementary Lessons in Electricity and Magnetism," p. 193, Macmillan, London (1899).
(*b*) W. L. BRAGG, "Electricity," p. 51, Bell, London (1936).
(*c*) G. W. VINAL, "Primary Batteries," p. 9, John Wiley & Sons, Inc., New York (1950).
5. T. H. PRATT, *Electronic Eng.*, **20**, 314 (1948).
6. A. ELLIOTT, *Electronic Eng.*, **20**, 317 (1948).

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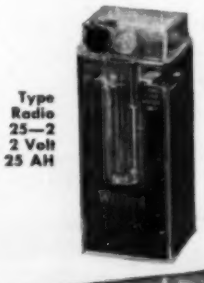

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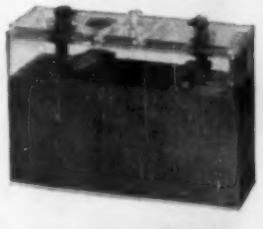

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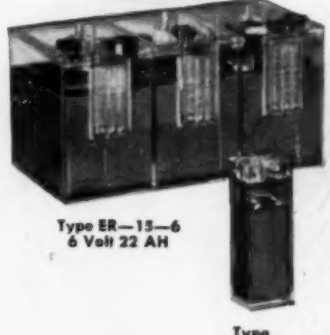

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